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SOIL SCIENCE

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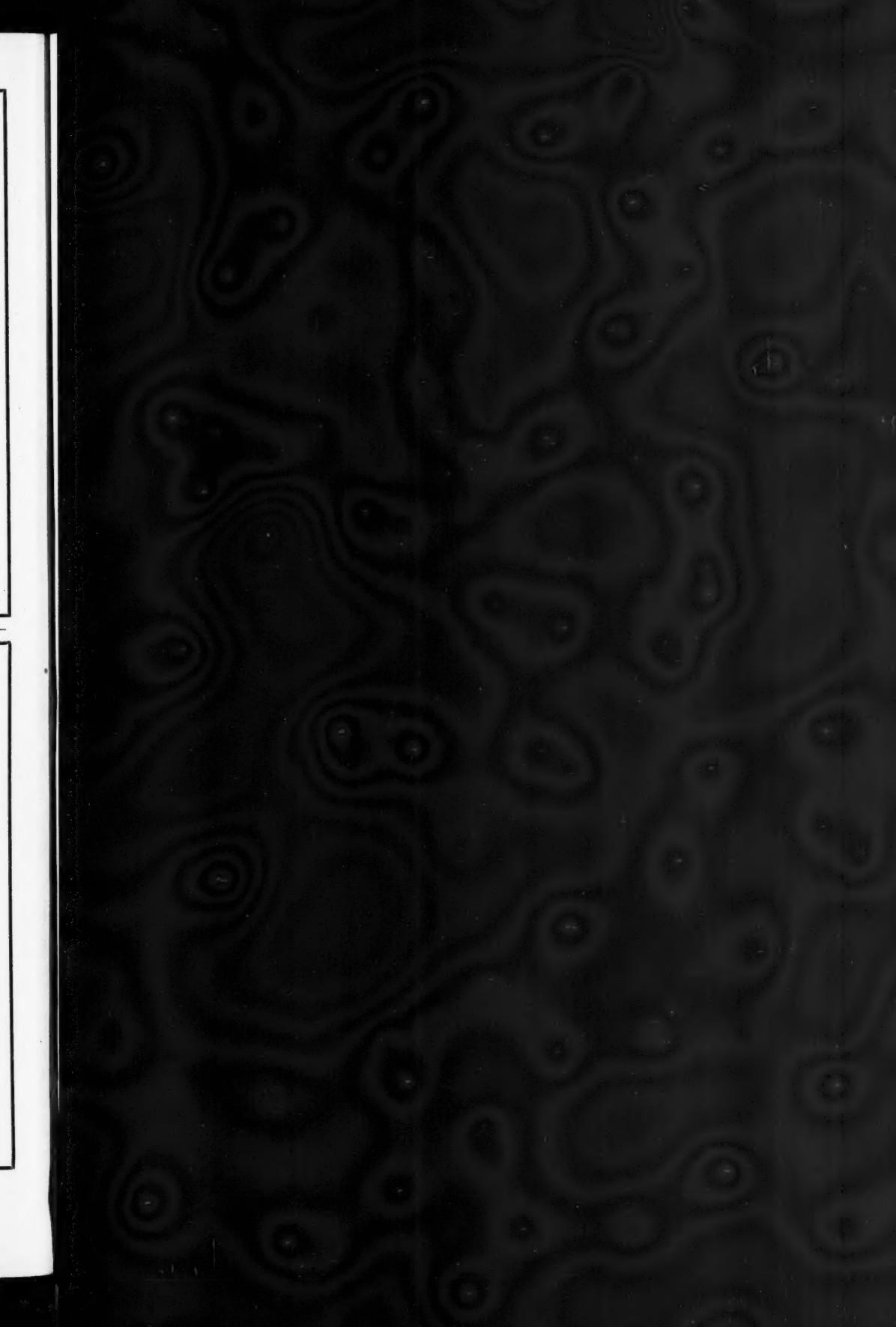
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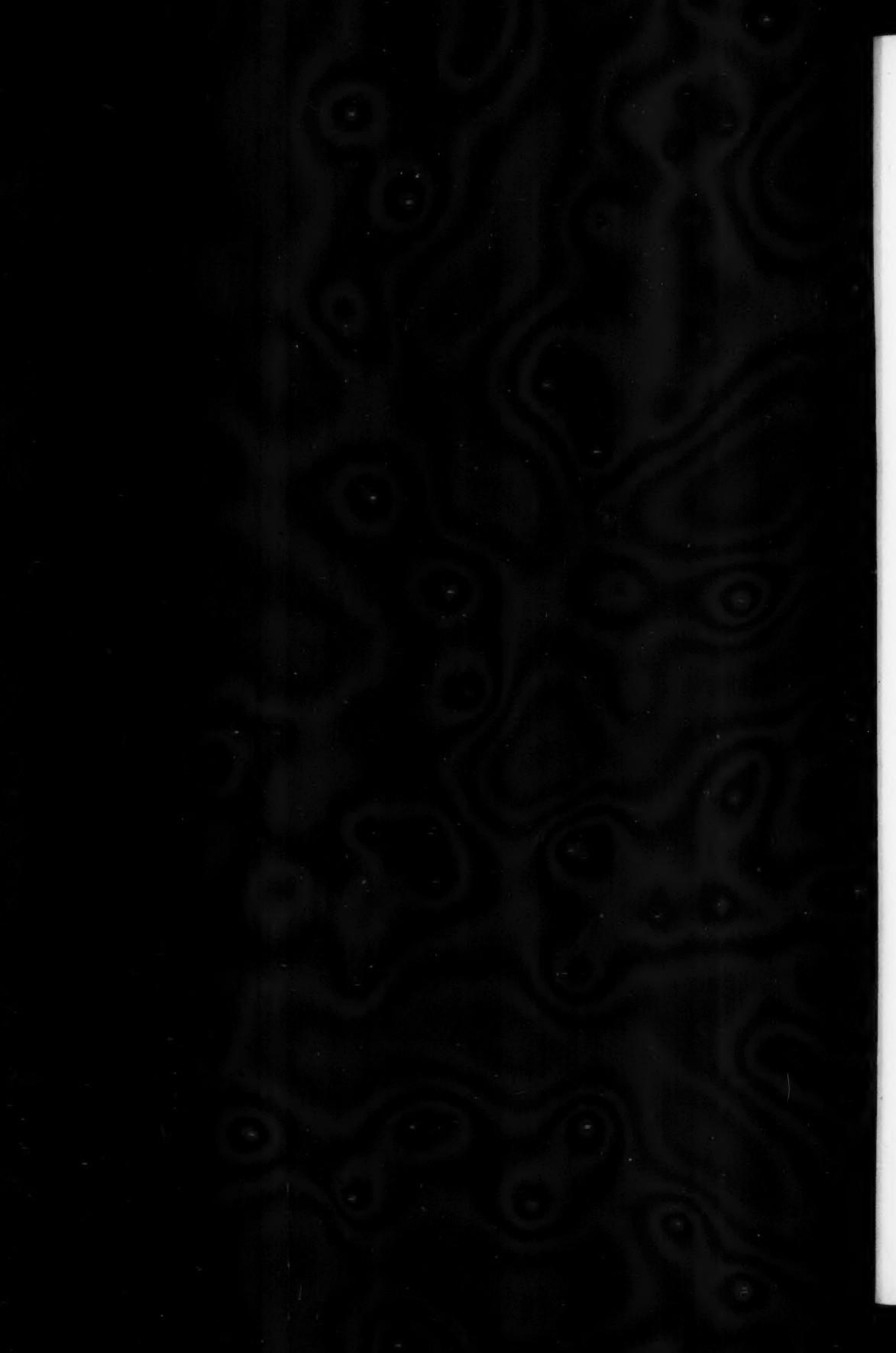
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## INFLUENCE OF ORGANIC MATTER UPON THE DEVELOPMENT OF FUNGI, ACTINOMYCETES AND BACTERIA IN THE SOIL<sup>1</sup>

SELMAN A. WAKSMAN AND ROBERT L. STARKEY

*New Jersey Agricultural Experiment Stations*

Received for publication January 22, 1924

It is a matter of common knowledge that the addition of organic matter to the soil greatly increases the development of microorganisms. It has also been recorded that the nature of the organic matter added influences not only the number of microorganisms but also the types developing in the soil.

We need cite only a few investigations on this subject. Engberding (4) found that the addition of 2 per cent of cane sugar to a soil brought about an increase of 1000 to 1500 per cent in the number of bacteria developing upon Heyden agar; addition of 0.5 per cent of dextrose brought about an increase of only 300-400 per cent. This increase was soon followed by a decrease and in some cases there were no more bacteria in the treated than in the control soils after two and one-half months. The addition of straw and green manure to the soil also increased the numbers of bacteria 300-600 per cent over the control. Stable manure and urine were also found to favor greatly the development of bacteria.

According to Bazarevski (1), the addition of dextrose to the soil increases the number of bacteria but diminishes the number of fungi, both in the presence and absence of available nitrogen salts. It was suggested that this may be due to the formation of a dry pellicle of sugar on the surface of soil preventing the admission of oxygen. Cellulose, however, greatly favored the development of fungi causing increases of 200-1000 per cent, and also favorably influenced the development of bacteria, especially in the presence of ammonium salts. Hiltner and Störmer (5), Conn (2) and others pointed out the fact that the addition of plant material increases the development of actinomycetes. Conn (3) found that fresh manure affects the development of the non-spore forming bacteria, but not of the spore formers.

The following data were obtained from studies concerned with the course of decomposition, in the soil, of organic substances of varying carbon-nitrogen ratio. The common plate method was used for the determination of the numbers. Bacteria and actinomycetes were determined on albumin agar (7). A special acid medium, described elsewhere (6), was used for the determination of fungi. Dextrose (0.5 per cent), cellulose (1 per cent filter paper) with and without soluble nitrogen (0.1 per cent NaNO<sub>3</sub>), rye straw (1 per cent), alfalfa meal (1 per cent) and dried blood (1 per cent) were used as sources of organic matter. Thus a series of organic substances of varying nitrogen content were used; viz., dextrose and cellulose (free from nitrogen), straw (0.7 per cent nitrogen), alfalfa meal (2.5 per cent nitrogen), and dried blood (9.5 per cent nitrogen). The numbers of microorganisms in the soil

<sup>1</sup> Paper No. 163 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

developing as a result of the addition of organic matter were determined ten to seventeen days after the addition of the organic matter, except in the case

TABLE 1  
*Treatment of soils used in the experiments*

| SOIL NUMBER | ANNUAL TREATMENT   | pH  | FERTILITY    | NITRATE-N IN 100 GM. OF SOIL INCUBATED FOR 20 DAYS<br>mgm. |
|-------------|--|-----|--------------|--|
| 5A          | Manure, minerals*  | 5.5 | Very fertile | 1.80   |
| 5B          | Manure, lime, minerals*  | 6.7 | Very fertile | 1.55   |
| 7A          | Untreated  | 5.1 | Very poor    | 0.59   |
| 7B          | Lime alone   | 6.5 | Fair         | 0.66   |
| 9A          | NaNO <sub>3</sub> , minerals                                     | 5.8 | Good         | 1.05   |
| 11B         | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , minerals, lime | 6.0 | Good         | 1.01   |

\* Minerals = potassium salt and phosphate.

TABLE 2  
*Influence of 0.5 per cent dextrose upon the development of microorganisms in the soil after 2 days*

| SOIL NUMBER | FUNGI   |         | BACTERIA + ACTINOMYCETES |           | ACTINOMYCETES |       |
|-------------|---------|---------|--------------------------|-----------|---------------|-------|
|             | Start   | End     | Start                    | End       | Start         | End   |
|             |         |         | thousands                | thousands |               |       |
| 5A          | 87,300  | 109,400 | 6,500                    | 43,000    | 1,800         | 3,000 |
| 5B          | 19,700  | 24,000  | 9,360                    | 103,000   | 3,360         | ..... |
| 7A          | 115,700 | 82,000  | 3,860                    | 22,200    | 1,260         | 1,940 |
| 7B          | 20,000  | 25,400  | 7,760                    | 22,000    | 2,760         | ..... |
| 9A          | 73,300  | 102,000 | 8,000                    | 47,400    | 1,500         | 1,740 |
| 11B         | 25,700  | 36,000  | 8,400                    | 30,880    | 2,700         | 2,880 |

TABLE 3  
*Influence of 1 per cent cellulose, with and without NaNO<sub>3</sub>, upon the development of microorganisms in the soil after 17 days*

| SOIL NUMBER | NaNO <sub>3</sub><br>per cent | FUNGI   |           | BACTERIA + ACTINOMYCETES |           | ACTINOMYCETES |       |
|-------------|-------------------------------|---------|-----------|--------------------------|-----------|---------------|-------|
|             |                               | Start   | End       | Start                    | End       | Start         | End   |
|             |                               |         |           | thousands                | thousands |               |       |
| 5A          | 0                             | 87,300  | 320,000   | 6,500                    | 21,400    | 1,800         | 6,400 |
| 5A          | 0.1                           | 87,300  | 3,100,000 | 6,500                    | 40,600    | 1,800         | 4,600 |
| 7A          | 0                             | 115,700 | 160,000   | 3,860                    | 3,600     | 1,260         | 600   |
| 7A          | 0.1                           | 115,700 | 4,800,000 | 3,860                    | 4,800     | 1,260         | 400   |
| 7B          | 0                             | 20,000  | 47,000    | 7,760                    | 17,400    | 2,760         | 2,200 |
| 7B          | 0.1                           | 20,000  | 290,000   | 7,760                    | 47,200    | 2,760         | 3,200 |

of dextrose when a 48-hour period of incubation was used. The soil was kept at optimum moisture content at 25–28°C. It was desirable to use short

periods of incubation since the most active decomposition and the greatest changes in the numbers and types of microörganisms occur shortly after adding the organic materials.

The soil used was a sassafras gravelly loam from a series of plots, whose fertility, physical, chemical and biological conditions have been modified as

TABLE 4

*Influence of rye straw (1 per cent) upon the development of microörganisms in the soil after 10 days:*

| SOIL NUMBER | FUNGI   |         | BACTERIA + ACTINOMYCETES |                  | ACTINOMYCETES    |                  |
|-------------|---------|---------|--------------------------|------------------|------------------|------------------|
|             | Start   | End     | Start                    | End              | Start            | End              |
|             |         |         | <i>thousands</i>         | <i>thousands</i> | <i>thousands</i> | <i>thousands</i> |
| 5A          | 87,300  | 750,000 | 6,500                    | 21,800           | 1,800            | 2,800            |
| 5B          | 19,700  | 24,000  | 9,360                    | 29,900           | 3,360            | 2,800            |
| 7A          | 115,700 | 600,000 | 3,860                    | 25,200           | 1,260            | 200              |
| 7B          | 20,000  | 19,000  | 7,760                    | 24,400           | 2,760            | 1,900            |
| 9A          | 73,300  | 650,000 | 8,000                    | 23,000           | 1,500            | 1,800            |
| 11B         | 25,700  | 47,000  | 8,400                    | 26,000           | 2,700            | 1,800            |

TABLE 5

*Influence of rye straw (0.5 per cent) and alfalfa meal (0.5 per cent), with and without NaNO<sub>3</sub>, upon the development of microörganisms in the soil after 14 days*

| TREATMENT OF SOIL                                | FUNGI   | BACTERIA + ACTINOMYCETES |
|--|---------|--------------------------|
| Untreated.....                                   | 38,700  | 8,875,000                |
| Straw.....                                       | 136,000 | 34,200,000               |
| Straw + 0.025 per cent NaNO <sub>3</sub> .....   | 233,000 | 35,700,000               |
| Alfalfa.....                                     | 297,000 | 74,600,000               |
| Alfalfa + 0.025 per cent NaNO <sub>3</sub> ..... | 247,000 | 73,400,000               |

TABLE 6

*Influence of dried blood (1 per cent) upon the numbers of microörganisms in the soil after 12 days*

| SOIL NUMBER | FUNGI   |           | BACTERIA + ACTINOMYCETES |                  | ACTINOMYCETES    |                  |
|-------------|---------|-----------|--------------------------|------------------|------------------|------------------|
|             | Start   | End       | Start                    | End              | Start            | End              |
|             |         |           | <i>thousands</i>         | <i>thousands</i> | <i>thousands</i> | <i>thousands</i> |
| 5A          | 87,300  | 2,079,950 | 6,500                    | 381,600          | 1,800            | 190,900          |
| 5B          | 19,700  | 73,300    | 9,360                    | 373,000          | 3,360            | 6,000            |
| 7A          | 115,700 | 1,438,300 | 3,860                    | 473,900          | 1,260            | 2,200            |
| 7B          | 20,000  | 125,000   | 7,760                    | 352,700          | 2,760            | 500              |
| 9A          | 73,300  | 1,871,650 | 8,000                    | 312,200          | 1,500            | 128,700          |
| 11B         | 25,700  | 311,600   | 8,400                    | 107,900          | 2,700            | 42,700           |

a result of fertilizer treatments for the last fifteen years. Table 1 indicates the treatments and present conditions of these soils.

The results given in tables 2-6 indicate the effects of various organic substances upon the development of microörganisms in these soils.

These studies confirmed the previous observations of Engberding, Bazarevski and others that dextrose increases primarily the development of bacteria, but not of fungi and actinomycetes. This is due to several factors:

1. The majority of bacteria use dextrose in preference to higher carbohydrates and their derivatives, while many fungi readily decompose celluloses, pentoses, and other complex carbohydrates.

2. Bacteria generally require much less nitrogen for the synthesis of their cells per unit of dextrose decomposed than do the fungi, the latter producing an abundant mycelium, for which considerable nitrogen is required.

3. Among the bacteria, the nitrogen-fixing forms readily utilize dextrose as a source of energy without requiring any combined nitrogen. Bacteria develop rapidly following the addition of dextrose, in the presence of even a small amount of available nitrogen while the fungi, which require a large amount of available nitrogen, or the actinomycetes, which develop only very slowly, may not be affected to any appreciable extent. It is interesting to note that the smallest increase in numbers occurred in the two poorest soils (7A and 7B), and the greatest increase in the fertile nearly neutral soil (5B).

Cellulose in particular, affected an entirely different group of microorganisms than did the dextrose, although both are pure carbohydrates, free from any traces of nitrogen. Cellulose is not attacked at all by most soil bacteria, but is very readily acted upon by numerous soil fungi. Even in the case where there was an increase in the number of bacteria following the addition of cellulose, the great increase in the number of fungi makes us wonder whether the multiplication of bacteria is due entirely to the utilization of the cellulose directly or in part to the utilization of its decomposition products. Where no nitrogen was added, the greatest increase of fungi and of bacteria took place in the fertile acid soil (5A), followed by poor acid soil (7A), for fungi, and by the poor neutral soil (7B), for bacteria. When  $\text{NaNO}_3$  is added, there was a ten-fold increase of the fungi in the fertile acid soil, over the soil to which no  $\text{NaNO}_3$  has been added, and a thirty-fold increase in the poor acid soil. The addition of  $\text{NaNO}_3$  brought about only a two-to three-fold increase in the number of bacteria over the numbers occurring where no  $\text{NaNO}_3$  was added. This again indicates the importance of the presence of available nitrogen for the development of fungi and for the decomposition of cellulose. The failure of the bacteria and actinomycetes to develop in the poor acid soil may be due to the original acid condition of the soil further slightly augmented by the acid formed from the cellulose by the fungi.

Straw contains a small amount of nitrogen (about 0.7 per cent), which may be sufficient for the needs of bacteria, but is not sufficient for an abundant development of fungi. Practically the same development of bacteria took place in all soils, with or without the addition of available nitrogen. The fungi, however, developed abundantly in the acid soils, but not in the limed soils; the addition of available nitrogen greatly increased the development of fungi (table 5) even in the case of straw.

Alfalfa increased the numbers of both bacteria and fungi to a much greater extent than did straw. Since alfalfa contains sufficient nitrogen (2.5 per cent) for the development of fungi, the addition of  $\text{NaNO}_3$  effected no increase in bacteria, nor even in fungi.

Dried blood, containing 9.5 per cent nitrogen, added to the soil brought about an entirely different development of the microorganisms than did the substances poor in protein. The numbers of bacteria were greatly increased in all soils, which points again to the fact that bacteria prefer protein substances (outside of dextrose and other readily available carbohydrates) as sources of energy, while the fungi can thrive upon both proteins and higher carbohydrates at the proper reaction. Fungi developed most abundantly in the acid soils and to a lesser extent in the limed soils. The actinomycetes developed most markedly in the two well buffered acid soils (5A, 9A). The lack of development of actinomycetes in the two poor soils (7A, 7B) and in the limed fertile soil (5B) is probably caused by the ammonia formed in abundance from one per cent of dried blood added. This made the reaction so alkaline ( $\text{pH} = 9.0$ ) in the two poor soils (poorly buffered) and in the neutral fertile soil that it repressed the development of actinomycetes, which are rather sensitive to extreme alkalinity as well as acidity.

#### SUMMARY

The observed effects of organic materials (dextrose, cellulose, rye straw, alfalfa meal, and dried blood) on the numbers of microörganisms in the soil, as determined by the plate method within three weeks after adding the materials, lead to the following conclusions:

1. All of the organic materials used greatly increase the numbers of microorganisms in the soil but not all to the same extent.
2. Some organic materials greatly affect one group of microörganisms but the others to a much less extent:
  - a. Dextrose increases the numbers of bacteria in particular.
  - b. Cellulose increases the numbers of fungi in particular.
  3. Rye straw and alfalfa meal increase the numbers of fungi and bacteria.
  4. Dried blood increases the fungi, bacteria and actinomycetes.
  5. Additions of  $\text{NaNO}_3$  to the straw treated soil further increase the numbers of fungi without affecting the numbers of bacteria. Nitrate additions greatly increase the development of microörganisms in soils treated with cellulose over those soils having no additions of nitrate.
  6. Alfalfa increases the numbers of microörganisms to a greater extent than straw, while dried blood causes greater increases than both of these.
  7. The numbers of fungi increase more abundantly in the acid soils than in those more nearly neutral in reaction.
  8. The numbers of microörganisms reach a much higher point in the fertile than in the less fertile soils.

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## MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY. IX. NITROGEN FIXATION AND MANNITE DECOMPOSITION<sup>1</sup>

SELMAN A. WAKSMAN AND P. D. KARUNAKAR

*New Jersey Agricultural Experiment Stations*

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Various investigators have reported that a definite correlation exists between the capacity of the soil to fix nitrogen and soil productivity, and also between this capacity and other bacterial activities, such as nitrification.

Christensen (6, 7), using as an index the intensity of growth of raw cultures of Azotobacter in mannite solutions inoculated with soil, came to the conclusion that this relative growth can serve as an index of the calcium and phosphorus content of the soil. Löhnis and Pillai (16) concluded that the fixation of nitrogen in mannite solutions inoculated with soil, is an approximate measure of the fertility of the soil, especially as to its content of available minerals. There was, however, no strict parallelism between the laboratory results and crop yields. Similar results were obtained by Moll (17) and Pillai (19).

Brown (3, 4) found that the results obtained from studies of nitrogen-fixation in soils, taken from plots subjected to different rotations, correlated very well with the results secured in the ammonification and nitrification tests as well as with crop yields. Brown concluded, therefore, that the nitrogen-fixing power of a soil may indicate its relative crop-producing power. A remarkable correlation between the amount of nitrogen fixed in 100 cc. of sterile mannite solution containing 1 gm. of mannite and inoculated with 1 gm. of soil and incubated for three weeks, with the known fertility of the soil was also observed by Burgess (5). He suggested, therefore, that next to nitrification, nitrogen-fixation tests can be used as criteria of soil fertility. Azotobacter was present in the more fertile soils and absent in the soils of low productivity.

Given, Kuhlman and Kern (12) also obtained a correlation between nitrogen fixation, in a solution of 2 per cent mannite, and crop productivity of a series of plots. However, on repeating the same experiment, with another series of plots, very little correlation was obtained. Beijerinck (1) suggested recently that there is a definite parallelism between the number of Azotobacter cells in the soil and soil fertility.

Two methods have been commonly used for determining the capacity of a soil to fix nitrogen; viz., the solution method and the soil method. The solution method was introduced by Remy (20, 21, 22) and further developed by Löhnis (15), and others. As applied to the measurement of the power of a soil to fix nitrogen, this method consists of adding 5-10 gm. of soil to 100 cc. of a standard nitrogen-free sterile mannite solution, incubating for 7-30 days, and then determining the amount of nitrogen fixed. By the use of this method, the activities of the nitrogen-fixing flora of the soil are studied under standard conditions, while the influence of the various physical and chemical conditions of the soil upon the activities of the organisms in the particular soil is not considered. The soil method consists

<sup>1</sup> Paper No. 166 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

in adding a certain amount of energy material (1-2 per cent mannite or dextrose) to 100 gm. of fresh soil placed in tumblers or flasks; the optimum amount of moisture is then added and the tumblers are incubated at a definite temperature for 21-30 days, when the increase in total nitrogen is determined. The advantage of the soil method is supposed to consist in the fact that the fixation of nitrogen is studied under conditions similar to those that take place in a natural soil, where the activities of the organisms are more normal. Both of these methods are, of course, far from imitating natural conditions, since one can hardly imagine a soil to which 1 or 2 per cent of soluble organic nitrogen-free material is added. According to Green (13), the solution method proves to be valuable in the study of the fixation of nitrogen, while Brown (3) considered the soil method as an improvement over the solution method.

The underlying principle of the two methods, for the study of the fixation of nitrogen can thus be summarized as follows:

A source of energy, chiefly mannite or dextrose, is added to the soil or to a solution inoculated with soil. The amount of available nitrogen in the soil is very limited, so that the fungi and heterotrophic non-nitrogen fixing bacteria, which are capable of consuming rapidly the mannite or dextrose, cannot do that to a very large extent, since a minimum of nitrogen is required for their growth. The amount of dextrose or mannite used in the laboratory tests (1 to 2 per cent) is in great excess over the amount of available nitrogen, present in the soil or solution. Since the nitrogen-fixing bacteria can readily utilize mannite or dextrose and fix atmospheric nitrogen, in the absence of available nitrogen, the excess of the former will enable them to fix the nitrogen. This has been demonstrated by Waksman and Starkey (24), who found that cellulose and substances rich in cellulose, like straw, greatly stimulate the development of fungi, especially in the presence of available nitrogen. The addition of dextrose to the soil will not, however, greatly affect the development of these organisms, but will stimulate greatly the multiplication of bacteria, especially the nitrogen-fixing forms.

Lipman and Burgess (14) have shown that, with a proper supply of energy-producing materials, all agricultural soils may be made to fix atmospheric nitrogen, when inoculated into a properly constituted mannite solution; only a fraction of these soils, however, contain Azotobacter organisms; soils containing the latter possessed a greater nitrogen-fixing power. In this connection, the reaction of the soil, as expressed by its hydrogen-ion concentration, is of prime importance, both in influencing the development of particular types of nitrogen-fixing bacteria and in the amount of nitrogen that will be fixed per gram of mannite or dextrose consumed. At a pH value of 6.0 and above, Azotobacter will develop in the soil; at a greater acidity, other nitrogen-fixing bacteria, like the Clostridium group and perhaps the *B. aerogenes* and *B. asterosporus* groups, will develop. It seems that the latter are less efficient than Azotobacter in fixing atmospheric nitrogen. Gainey (11), for example, has demonstrated that out of 418 soils examined, 199 were found to contain Azotobacter; the average amount of nitrogen fixed, per gram of sugar, was 6.36 mgm. for all soils, 8.30 mgm. for those containing Azotobacter, and 4.61 mgm. for those not containing any Azotobacter.

The nitrogen-fixing bacteria are, however, limited in their activities by one mineral, which they require in excess over the others, namely phosphorus. Stoklasa (23), for example, has shown that the Azotobacter cells contain as much as 5 per cent  $P_2O_5$ . When an excess of mannite or glucose is added to the soil or solution, the Azotobacter, Clostridium and other nitrogen-fixing bacteria will make an extensive growth, using the available energy and deriving their nitrogen from the atmosphere. Since about one unit of available phosphorus ( $P_2O_5$ ) is required for every two units of nitrogen fixed or assimilated by the organisms and synthesized into microbial protein, the supply of phosphorus may be a limiting factor. The actual amount of nitrogen fixed in the soil, especially by Azotobacter, may then become merely an index of the available phosphorus in the soil.

Dzierzbiczki (9) attempted to determine the need of phosphorus in the soil by the development of Azotobacter. Niklewski (18) added 10 gm. of soil to 100 cc. of a solution containing mannite, with or without soluble phosphate; the solution was sterilized either before or after adding the soil, and inoculated with Azotobacter. The following results were obtained:

*Nitrogen fixed in 100 cc. of mannite solution + 10 gm. of soil*

| SOIL NEED OF PHOSPHORUS | SOLUTION STERILIZED BEFORE SOIL WAS ADDED |  | SOLUTION STERILIZED AFTER SOIL WAS ADDED |  |
|-------------------------|---|--|--|--|
|                         | P <sub>2</sub> O <sub>5</sub> in medium   | No P <sub>2</sub> O <sub>5</sub> in medium | P <sub>2</sub> O <sub>5</sub> in medium  | No P <sub>2</sub> O <sub>5</sub> in medium |
| None.....               | 8.22                                      | 5.35                                       |  | 2.85                                       |
| Medium.....             | 5.48                                      | 4.08                                       | 14.51                                    | 1.95                                       |
| Great.....              | 3.78                                      | 1.67                                       | 15.05                                    | 0.35                                       |

Stoklasa (23) used the following method for determining the need of the soil for phosphorus: 30 cc. of water containing 2.5 gm. of glucose, 0.2 gm. K<sub>2</sub>SO<sub>4</sub> and 0.05 gm. of MgCl<sub>2</sub> were added to 100 gm. of soil; the soil was then sterilized and inoculated with Azotobacter. After 21 days of incubation, the total nitrogen and phosphoric acid were determined in the soil. One hundred grams of soil was found to contain 0.103 gm. of P<sub>2</sub>O<sub>5</sub> and 0.164 gm. of nitrogen in the inoculated soil and 0.110 gm. of nitrogen in the uninoculated soil. The amount of nitrogen fixed was, therefore, 0.054 gm. Since Azotobacter cells contain 10 per cent nitrogen and 5 per cent P<sub>2</sub>O<sub>5</sub>, 0.027 gm. P<sub>2</sub>O<sub>5</sub> or 26.21 per cent of the total P<sub>2</sub>O<sub>5</sub> in the soil had to be assimilated by Azotobacter. This is an index of the available fraction of phosphorus in the soil.

A very fertile soil containing 0.084 per cent P<sub>2</sub>O<sub>5</sub> has shown, by the above method, that 48.8 per cent of the total phosphorus was available; a soil of medium fertility contained 26.21 per cent available P<sub>2</sub>O<sub>5</sub> out of a total content of 0.103 per cent, while only 11.66 per cent of the P<sub>2</sub>O<sub>5</sub> of a poor forest soil was available out of a total content of 0.090 per cent.

Christensen (7) employed a phosphorus-free mineral solution, containing some CaCO<sub>3</sub> and 0.3 gm. KCl, to which he added 10 per cent of soil (5 gm. of soil to 50 cc. of solution) and estimated, from the amount of Azotobacter growth, the amount of available phosphorus in the soil. But in view of the fact that there are only few soils which are capable of allowing the development of Azotobacter in phosphorus-free mannite solution, the test should be modified so as to be sensitive to smaller differences in the content of available phosphorus in the soil. This is accomplished by using a series of flasks (10 or 11) containing mannite solution and varying amounts of K<sub>2</sub>HPO<sub>4</sub> (0.0005 to 0.005 mgm.) and record is made of the concentration of phosphorus at which Azotobacter development takes place and where it reaches a maximum. Different soils were found to behave differently in this respect, so that even this test did not give the absolute phosphorus requirement of the soil. However, abundant Azotobacter development in phosphorus-free mannite solution indicates that the soil does not need any phosphorus.

Christensen (8) has further shown that the power of a soil to decompose mannite depends primarily on the differences in the chemical condition of the soil. In the case of neutral or alkaline soils, the power to decompose mannite depends on the presence of available phosphates. The speed of decomposition of mannite in neutral soils may indicate, therefore, the need of a soil in available phosphates.

The method used by Christensen (8) and finally modified by Bondorff and Christensen (2) was carried out as follows:

One hundred grams of air-dry soil and 2 gm. of mannite are well mixed, placed in tumblers and brought up to moisture with distilled water. After the tumblers have been allowed to

stand undisturbed for 2-3 hours, the soil is well stirred with a glass spatula and incubation at 25°C. is started. At intervals of five days, 5 gm. of soil is withdrawn and allowed to air-dry; the air-dry soil is then weighed again and extracted for two hours, with occasional shaking, with 200 cc. of water. The extract is then filtered through paper and 10 cc., or an amount equivalent to 0.25 gm. of soil, is placed in a 400-cc. beaker with 50 cc. of 0.05 N potassium permanganate solution and 3 cc. of dilute (6:100) sulfuric acid. The beaker is placed in boiling water for twenty minutes. Fifty cubic centimeters of 0.05 N oxalic acid is then added and the solution is titrated with 0.02 N potassium permanganate solution. The number of cubic centimeters of permanganate solution required indicates the amount of organic matter (residual mannite + soluble soil organic matter).

These methods for determining the nitrogen-fixing as well as the mannite-decomposing power of a soil can thus be divided into four groups:

1. The addition of mannite (usually 1-2 per cent) to the soil, incubating for 15-30 days, under optimum conditions, then measuring the increase in the total nitrogen of the soil.
2. Inoculation of a mannite solution, usually containing phosphate, sulfate,  $\text{CaCO}_3$  and 1-2 per cent mannite, with 1-10 per cent of the fresh soil, incubating for 15-30 days, then determining the amount of nitrogen fixed.
3. Adding 10 per cent of soil to a phosphate-free mannite solution and incubating, or sterilizing and inoculating with Azotobacter and incubating, for 20-30 days, then determining the amount of nitrogen fixed.
4. Proceeding as in the first method, but determining at intervals of five days, for a period of thirty days, the residual mannite or content of soluble organic matter, by the potassium permanganate method or by any other method.

All these methods are based upon the principle pointed out above that an excess of an available carbohydrate, like mannite, will stimulate only organisms that can rapidly decompose the excess of mannite and obtain their nitrogen from the atmosphere. These organisms, will, therefore, fix a definite amount of nitrogen (depending also upon the nature of the organism) for a definite amount of mannite decomposed. The first and the fourth methods should, therefore, give the same results, only the latter may prove to be more sensitive. But since a large amount of available phosphorus is required for an extensive development of the nitrogen-fixing bacteria, especially the Azotobacter, and since there is a more or less definite correlation between the phosphorus and nitrogen content of the Azotobacter cells, the only limiting factor to the development of Azotobacter and other nitrogen-fixing bacteria and to the fixation of nitrogen (if there is enough potassium and calcium, and if the reaction is favorable), is the amount of available phosphorus in the soil, as indicated by method 3. The second method would merely indicate the type of nitrogen fixing flora existing in the soil, under the particular circumstances. A critical study of these four methods was therefore undertaken.

#### EXPERIMENTAL

A series of plots, treated for the last fifteen years with different fertilizers, which have been used in the previous studies reported in this series, were also employed for the following investigations. The treatment of the plots as well as their carbon and nitrogen content and crop yield is given in table 1.

In the first experiment (table 2) on nitrogen-fixation by different soils the tumbler or soil method was used:

One hundred-gram portions of the different soils, sampled on August 24, 1922, were placed in tumblers, 1 gm. of mannite was added to each, the soils were well mixed and, after the moisture was brought to 50 per cent of the moisture-holding capacity, the tumblers were incubated at 25–28°C. for thirty days. The total nitrogen was determined in the original soil and in the soil receiving mannite, by the Kjeldahl method, using 5 gm. of air-dry sieved soil.

TABLE 1  
*Chemical condition of the soil and crop yields*

| SOIL NUMBER | TREATMENT*  | NITROGEN CONTENT<br>per cent | CARBON CONTENT<br>per cent | REACTION<br>1922 | CROP YIELD        |                        |
|-------------|---|------------------------------|----------------------------|------------------|-------------------|------------------------|
|             |   |                              |                            |                  | 1908–1922<br>lbs. | 1923<br>(corn)<br>lbs. |
| 5A          | Minerals + manure   | 0.1463                       | 1.73                       | 5.5              | 69,300            | 6,108                  |
| 7A          | Untreated   | 0.0826                       | 0.96                       | 4.9              | 15,464            | 1,710                  |
| 9A          | Minerals + NaNO <sub>3</sub>                                      | 0.0994                       | 1.17                       | 5.8              | 57,968            | 5,273                  |
| 11A         | Minerals + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>        | 0.1064                       | 1.23                       | 4.4              | 41,754            | 1,753                  |
| 19A         | Minerals only   | 0.0908                       | 1.13                       | 5.4              | 29,926            | 5,030                  |
| 5B          | Minerals + manure + lime  | 0.1428                       | 1.74                       | 6.7              | 59,754            | 6,478                  |
| 7B          | Lime only   | 0.0868                       | 1.18                       | 6.5              | 30,160            | 5,566                  |
| 11B         | Minerals + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + lime | 0.0952                       | 1.10                       | 5.9              | 61,906            | 6,440                  |
| 19B         | Minerals + lime   | 0.0924                       | 1.18                       | 6.4              | 35,930            | 6,043                  |

\*Minerals = Yearly applications of 640 pounds acid phosphate and 320 pounds of potassium chloride per acre.

Manure = 32 tons of cow manure per acre.

Lime = 2 tons of ground lime every 5 years.

NaNO<sub>3</sub> = 320 pounds NaNO<sub>3</sub> per acre.

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = An amount equivalent to 320 pounds of NaNO<sub>3</sub>.

TABLE 2  
*Nitrogen-fixation in soils to which 1 per cent mannite has been added*

| SOIL NUMBER | NITROGEN IN SOIL ITSELF |          | NITROGEN IN SOIL + MANNITE |          |
|-------------|-------------------------|----------|----------------------------|----------|
|             | per cent                | per cent | per cent                   | per cent |
| 5A          | 0.1463                  |          | 0.1468                     |          |
| 7A          | 0.0826                  |          | 0.0784                     |          |
| 9A          | 0.0994                  |          | 0.0994                     |          |
| 11A         | 0.1064                  |          | 0.1076                     |          |
| 5B          | 0.1428                  |          | 0.1512                     |          |
| 7B          | 0.0868                  |          | 0.1316                     |          |
| 9B          | 0.1020                  |          | 0.1120                     |          |
| 11B         | 0.0952                  |          | 0.0952                     |          |

Table 2 indicates that the only definite differentiation that we may obtain in reference to nitrogen-fixation in the soil by the tumbler method, is influenced

by the soil reaction. All the soils with pH values less than 6.0 gave no increase or only a very slight increase in total nitrogen, while those soils having pH values greater than 6.0 gave a decided increase in the amount of total nitrogen. It is interesting to note that this is the limit for the development of Azotobacter in soils, as shown by Gainey (10). However, this method of

TABLE 3  
*Fixation of nitrogen in 100 cc. mannite solution inoculated with 5 gm. of soil\**

| SOIL NUMBER | CONTROL |  | INCUBATED |  | INCREASE IN NITROGEN |  |
|-------------|---------|--|-----------|--|----------------------|--|
|             | mgm.    |  | mgm.      |  | mgm.                 |  |
| 5A          | 8.20    |  | 10.80     |  | 2.60                 |  |
| 7A          | 4.96    |  | 7.12      |  | 2.16                 |  |
| 11A         | 6.28    |  | 8.93      |  | 2.65                 |  |
| 19A         | 5.26    |  | 8.78      |  | 3.52                 |  |
| 5B          | 7.86    |  | 17.00     |  | 9.14                 |  |
| 7B          | 5.28    |  | 9.94      |  | 4.66                 |  |
| 11B         | 5.24    |  | 12.53     |  | 7.29                 |  |
| 19B         | 5.16    |  | 9.60      |  | 4.46                 |  |

\*Soil sampled June 26, 1923.

TABLE 4  
*Influence of quantity of soil upon the amount of nitrogen fixed in mannite solution*

| SOIL NUMBER | JULY 14, 1923      |                               |         |                    |                               |         | SEPTEMBER 11, 1923 |                               |         |                    |                               |         |
|-------------|--------------------|-------------------------------|---------|--------------------|-------------------------------|---------|--------------------|-------------------------------|---------|--------------------|-------------------------------|---------|
|             | 1 gm. of soil      |                               |         | 5 gm. of soil      |                               |         | 1 gm. of soil      |                               |         | 5 gm. of soil      |                               |         |
|             | Total N in control | Total N in incubated solution | N fixed | Total N in control | Total N in incubated solution | N fixed | Total N in control | Total N in incubated solution | N fixed | Total N in control | Total N in incubated solution | N fixed |
|             | mgm.               | mgm.                          | mgm.    |
| 5A          | 1.65               | 6.05                          | 4.40    | 6.65               | 10.40                         | 3.75    | 1.88               | 6.49                          | 4.61    | 6.42               | 11.09                         | 4.67    |
| 7A          | 1.00               | 4.90                          | 3.90    | 3.40               | 6.20                          | 2.80    | 1.24               | 5.38                          | 4.14    | 4.53               | 8.93                          | 4.40    |
| 9A          |                    |                               |         |                    |                               |         | 1.41               | 5.86                          | 4.45    | 5.32               | 8.78                          | 3.46    |
| 19A         | 1.28               | 4.50                          | 3.22    | 4.80               | 8.40                          | 3.60    | 1.44               | 5.76                          | 4.32    | 4.48               | 8.50                          | 4.02    |
| 5B          | 1.55               | 10.10                         | 8.55    | 6.15               | 12.10                         | 5.95    | 1.86               | 10.72                         | 8.86    | 6.68               | 16.70                         | 10.02   |
| 7B          | 1.27               | 6.90                          | 5.63    | 4.75               | 9.10                          | 4.35    | 1.28               | 5.52                          | 4.24    | 4.74               | 8.60                          | 3.86    |
| 11B         |                    |                               |         |                    |                               |         | 1.37               | 4.90                          | 3.53    | 5.12               | 7.78                          | 2.66    |
| 19B         | 1.26               | 4.50                          | 3.24    | 4.70               | 8.20                          | 3.50    | 1.36               | 8.64                          | 7.28    | 4.98               | 10.08                         | 5.10    |

determining the nitrogen-fixing capacity of the soil allows no further differentiation between the differently treated soils. Repeated experiments with the same method using 2 per cent of mannite gave similar results.

The solution method was found to give a different set of results, somewhat more applicable for differentiation of the soil, as shown in table 3, where

a typical experiment is reported. The solution used had the following composition:

|   |          |
|---|----------|
| Mannite.....                              | 20.0 gm. |
| MgSO <sub>4</sub> ·7H <sub>2</sub> O..... | 0.2 gm.  |
| K <sub>2</sub> HPO <sub>4</sub> .....     | 0.2 gm.  |
| NaCl.....                                 | 0.2 gm.  |
| CaCO <sub>3</sub> .....                   | 5.0 gm.  |
| Distilled water.....                      | 1000 cc. |

Made neutral to phenolphthalein with NaOH

One hundred-gram portions of the sterile solution were placed in 250 cc. Erlenmeyer flasks, plugged, sterilized, inoculated with 5 gm. of soil and incubated for 15 to 30 days; the total nitrogen was then determined in the incubated solution + soil and in the check solution + soil.

Although the differences in the nitrogen-fixing capacity of the different soils were definite, they did not always correspond to the fertility of the soil. The correlation is much better in the limed plots (B), where the reaction is not as acid as in the unlimed plots (A). In the former, the order of nitrogen fixation is 5B, 11B, 7B and 19B. Table 1 shows that the crop yields of these respective plots were in about the same order. However, in the case of the unlimed soils, there is little differentiation, the soil of the most fertile plot 5A fixing less nitrogen than the soil of the most acid plot 11A and a trace more than the most unfertile soil 7A. There is no doubt, therefore, that this method can yield certain information on the microbiological condition of the soil, but it should be modified.

To determine the influence of the quantity of soil added to the mannite solution upon the amount of nitrogen fixed, 1 and 5 gm. quantities were used, as shown in table 4.

The results brought out in the above table tend to show that, although appreciable quantities of nitrogen are fixed in mannite solutions inoculated with various soils, we do not find any such sharp differentiation between the variously treated soils (especially in the case of unlimed soils), as was found by the methods previously studied, namely, numbers of microorganisms, nitrifying and CO<sub>2</sub>-producing capacities. All the unlimed soils possess about an equal nitrogen-fixing capacity as determined by the solution method. This may be due to the fact that all of them contain a similar nitrogen-fixing flora (with the exception of the B plots, especially 5B and 19B which contain Azotobacter as well); when introduced into a favorable medium of the same composition, equal amounts of nitrogen are, therefore, fixed.

The following experiment was carried out with the idea of establishing whether any of the soil constituents, especially the phosphates affect the amount of nitrogen fixed. In this case the composition of the soil itself, especially its phosphate content, is made the variable factor, and the organism used for the fixation of nitrogen is the same. Ten-gram portions of the various soils (in a moist condition) were added to 100-cc. portions of the

liquid medium, with or without the phosphate; the flasks were plugged with cotton and sterilized at 15 pounds pressure for 1.5 hours. Some of the cultures were inoculated with *Az. vinelandii* and some were left as controls. After twenty days of incubation, the amounts of nitrogen fixed were determined, as shown in table 5.

TABLE 5  
*Influence of different soils and available phosphorus upon nitrogen fixation by Azotobacter vinelandii*

| SOIL NUMBER | NITROGEN FIXED WITH PHOSPHORUS PRESENT IN MEDIUM |           |         | NITROGEN FIXED WITH PHOSPHORUS ABSENT IN MEDIUM |           |         |
|-------------|--|-----------|---------|---|-----------|---------|
|             | Control  | Incubated | N fixed | Control   | Incubated | N fixed |
|             | mgm.   | mgm.      | mgm.    | mgm.  | mgm.      | mgm.    |
| 5A          | 8.78   | 18.36     | 9.58    | 8.78  | 16.42     | 7.64    |
| 7A          | 5.33   | 10.66     | 5.33    | 5.33  | 7.92      | 4.59    |
| 9A          | 7.06   | 13.68     | 6.62    | 7.06  | 13.25     | 6.19    |
| 19A         | 7.06   | 14.11     | 7.05    | 7.06  | 13.68     | 6.62    |
| 5B          | 9.30   | 21.17     | 11.87   | 9.30  | 13.39     | 4.09    |
| 7B          | 5.03   | 15.70     | 10.67   | 5.03  | 8.35      | 3.32    |
| 19B         | 6.91   | 17.28     | 10.37   | 6.91  | 9.07      | 2.16    |

TABLE 6  
*Course of decomposition of 1 per cent mannite in soils of different fertility\**

| SOIL NUMBER | AFTER 2 DAYS' INCUBATION |                |            | AFTER 5 DAYS' INCUBATION |                |            | AFTER 7 DAYS' INCUBATION |                |            | AFTER 12 DAYS' INCUBATION |                |            |
|-------------|--------------------------|----------------|------------|--------------------------|----------------|------------|--------------------------|----------------|------------|---------------------------|----------------|------------|
|             | Soil alone               | Soil + mannite | Difference | Soil alone               | Soil + mannite | Difference | Soil alone               | Soil + mannite | Difference | Soil alone                | Soil + mannite | Difference |
|             |                          |                |            |                          |                |            |                          |                |            |                           |                |            |
| 5A          | 7.8*                     | 21.1           | 13.3       | 6.1                      | 18.0           | 11.9       | 6.7                      | 13.2           | 6.5        | 3.2                       | 5.5            | 2.3        |
| 7A          | 7.9                      | 21.2           | 13.3       | 4.7                      | 17.7           | 13.0       | 6.3                      | 18.0           | 11.7       | 3.1                       | 15.8           | 12.7       |
| 5B          | 8.3                      | 19.3           | 11.0       | 4.7                      | 13.9           | 9.2        | 4.6                      | 5.1            | 0.5        | 3.3                       | 4.8            | 1.5        |
| 7B          | 4.5                      | 18.9           | 14.4       | 9.6                      | 20.1           | 10.5       | 4.5                      | 15.7           | 11.2       | 2.1                       | 11.7           | 9.6        |

\*The figures in tables 6, 7, and 8 represent the cubic centimeters of 0.02 N permanganate solution used in neutralizing a solution, which was obtained by digesting 5 gm. of soil with 200 cc. of water, then digesting 10 cc. of the extract with 50 cc. of 0.05 N KMnO<sub>4</sub> solution, treating with 50 cc. 0.05 N oxalic acid and titrating with 0.02 N KMnO<sub>4</sub>.

The soils which brought about the largest amount of nitrogen-fixation by Azotobacter, in the presence of phosphorus, namely 5B, 7B, 19B, have shown the lowest nitrogen-fixation in the absence of phosphorus. This becomes clear when we consider the crop yields for 1923. The samples were taken on September 29, just after the corn crop was harvested. Since larger yields were obtained on plots 5B, 7B and 19B than on the corresponding A plots, one would expect that these soils should contain less available phosphates at that particular period and, if this is the factor limiting the amount of nitrogen fixed, the above results would be expected.

In the last experiment, the amounts of mannite left in the medium were determined by the method of Christensen and were found to run parallel with the amounts of nitrogen fixed.

TABLE 7  
*Course of decomposition of 2 per cent mannite in soils of different fertility\**

| SOIL NUMBER | TREATMENT   | INITIAL SAMPLE | AFTER 3 DAYS' INCUBATION | AFTER 13 DAYS' INCUBATION | AFTER 20 DAYS' INCUBATION | AFTER 35 DAYS' INCUBATION |
|-------------|---|----------------|--------------------------|---------------------------|---------------------------|---------------------------|
| 5A          |   | 42.3*          | 33.2                     | 30.8                      | 25.7                      | 13.0                      |
| 7A          |   | 41.9           | 39.2                     | 27.3                      | 29.9                      | 25.2                      |
| 19A         |   | 49.8           | 38.3                     | 29.1                      | 30.6                      | 26.1                      |
| 5B          |   | 44.8           | 30.7                     | 5.6                       | 3.6                       | 3.9                       |
| 7B          |   | 43.2           | 35.0                     | 26.1                      | 24.2                      | 17.3                      |
| 11B         |   | 43.1           | 31.5                     | 24.2                      | 28.7                      | 17.8                      |
| 19B         |   | 43.1           | 33.0                     | 21.8                      | 29.7                      | 26.6                      |
| 7A          | 25 mgm. K <sub>2</sub> HPO <sub>4</sub>                               | 41.9           | 33.9                     | 23.5                      | 23.6                      | 16.8                      |
| 7A          | 100 mgm. K <sub>2</sub> HPO <sub>4</sub>                              | 42.7           | 26.0                     | 23.6                      | 20.5                      | 7.8                       |
| 7A          | 100 mgm. K <sub>2</sub> HPO <sub>4</sub> + 100 mgm. CaCO <sub>3</sub> | 42.3           | 26.3                     | 20.8                      | 20.8                      | 8.3                       |

\* See footnote for table 6.

TABLE 8  
*Course of decomposition of 2 per cent mannite solution in differently treated soils and the influence of available phosphates\**

| SOIL NUMBER | TREATMENT   | INITIAL SAMPLE | INCUBATED 3 DAYS | INCUBATED 7 DAYS | INCUBATED 13 DAYS | INCUBATED 20 DAYS | INCUBATED 31 DAYS |
|-------------|---|----------------|------------------|------------------|-------------------|-------------------|-------------------|
| 5A          |   | 41.0*          | 29.9             | 29.1             | 18.2              | 6.4               | 8.4               |
| 7A          |   | 39.5           | 33.2             | 37.5             | 33.3              | 32.0              | 26.5              |
| 9A          |   | 39.5           | 34.4             | 33.9             | 27.8              | 22.4              | 14.4              |
| 11A         |   | 40.1           | 33.0             | 32.3             | 29.2              | 23.0              | 22.4              |
| 5B          |   | 41.4           | 29.8             | 20.1             | 9.5               | 4.3               | 6.5               |
| 7B          |   | 42.0           | 29.2             | 26.6             | 12.7              | 4.1               | 7.4               |
| 11B         |   | 38.1           | 29.4             | 26.3             | 20.3              | 14.8              | 7.0               |
| 5A          | 25 mgm. K <sub>2</sub> HPO <sub>4</sub>                               | 38.3           | 28.8             | 26.8             | 22.3              | 9.9               | 8.8               |
| 5A          | 100 mgm. K <sub>2</sub> HPO <sub>4</sub>                              | 35.5           | 25.8             | 25.4             | 19.6              | 7.5               | 8.5               |
| 5A          | 100 mgm. CaCO <sub>3</sub>  | 39.0           | 26.6             | 25.7             | 20.7              | 5.5               | 8.3               |
| 5A          | 100 mgm. CaCO <sub>3</sub> + 100 mgm. K <sub>2</sub> HPO <sub>4</sub> | 35.1           | 26.7             | 24.7             | 16.7              | 5.6               | 8.0               |
| 7A          | 25 mgm. K <sub>2</sub> HPO <sub>4</sub>                               | 39.1           | 30.0             | 33.9             | 31.3              | 30.8              | 21.3              |
| 7A          | 100 mgm. K <sub>2</sub> HPO <sub>4</sub>                              | 40.4           | 31.3             | 32.2             | 27.0              | 26.2              | 14.3              |
| 7A          | 100 mgm. CaCO <sub>3</sub>  | 42.0           | 28.7             | 31.2             | 27.2              | 26.8              | 15.0              |
| 7A          | 100 mgm. CaCO <sub>3</sub> + 100 mgm. K <sub>2</sub> HPO <sub>4</sub> | 38.5           | 28.9             | 32.4             | 27.3              | 19.4              | 8.6               |

\* See footnote for table 6.

To find whether the disappearance of mannite in the soil, as suggested by Christensen, may not prove to be a better index of the activities of the nitrogen-fixing bacteria than measuring the increase in nitrogen, 1 per cent man-

nite was added to a group of soils and the disappearance of mannite determined by the method of Bondorff and Christensen described above (table 6).

These results indicate that the fertile soils 5A and 5B, which contain sufficient phosphorus, decompose mannite very rapidly, especially the limed soil 5B; the unfertile soils 7A and 7B decompose mannite only slowly, especially

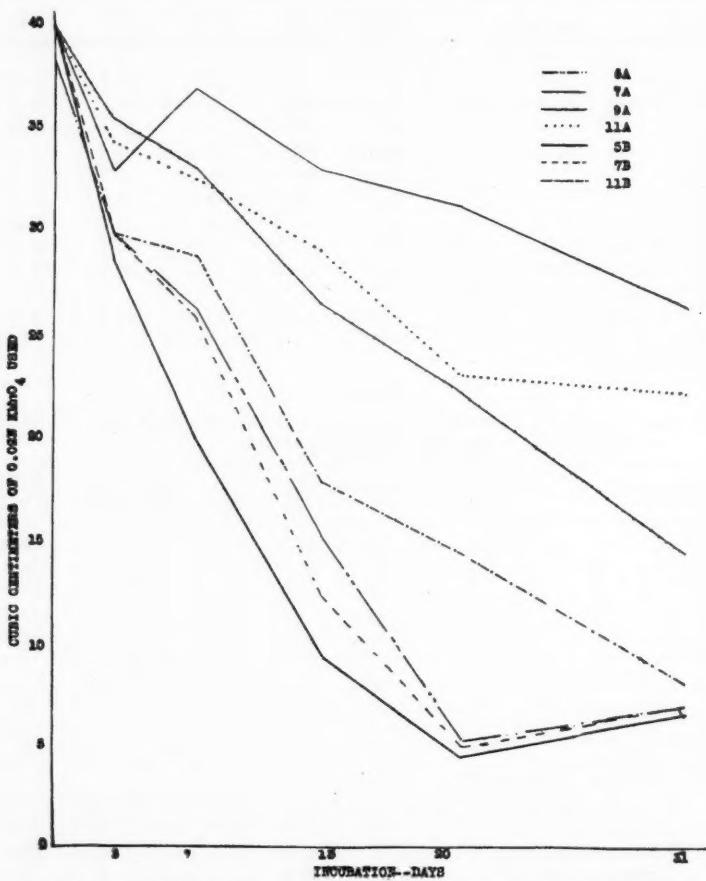


FIG. 1. COURSE OF MANNITE DECOMPOSITION IN SOILS OF DIFFERENT FERTILITY

the unlimed 7A. The experiment was repeated with a group of soils sampled on August 22, 1923, using 2 per cent mannite. To demonstrate whether the low mannite-decomposing capacity of 7A is due to the lack of phosphorus, to the acid reaction or to both, three groups of tumblers containing 100 gm. of soil 7A were treated (1) with 25 mgm.  $K_2HPO_4$ , (2) with 100 mgm.  $K_2HPO_4$

and (3) with 100 mgm.  $K_2HPO_4$  + 100 mgm.  $CaCO_3$ . The results are given in table 7.

Soils 5A and 5B are thus found to be most active in decomposing mannite; these soils receive both minerals and manure and are otherwise also most

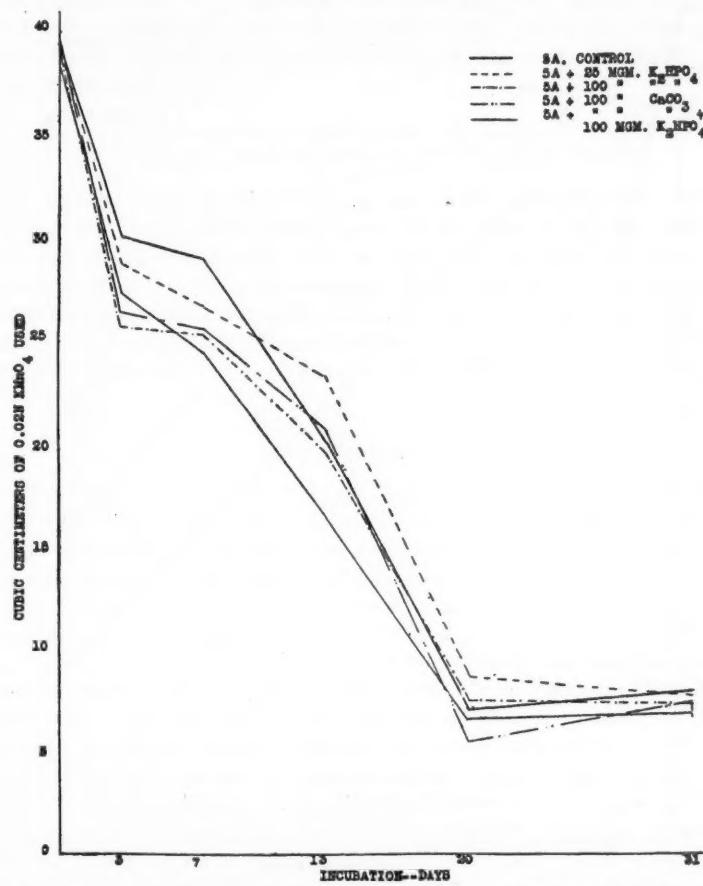


FIG. 2. INFLUENCE OF ADDITION OF SOLUBLE PHOSPHATE AND LIME TO A FERTILE ACID SOIL UPON ITS MANNITE-DECOMPOSING POWER

active biologically and most fertile. The most unfertile soil 7A, receiving no fertilizer or manure at all, and the soils receiving minerals only, but not nitrogenous fertilizer, were least active. The plots receiving lime only and lime, minerals and ammonium sulfate fell between these two groups of plots, in their mannite-decomposing power. The addition of 25 mgm.  $K_2HPO_4$

to 100 gm. of soil 7A was sufficient to greatly increase its mannite decomposing power. The addition of 100 mgm.  $K_2HPO_4$  brought about a still further action; the addition of  $CaCO_3$  to this acid soil, however, did not result in any greater activity than the addition of the phosphate alone.

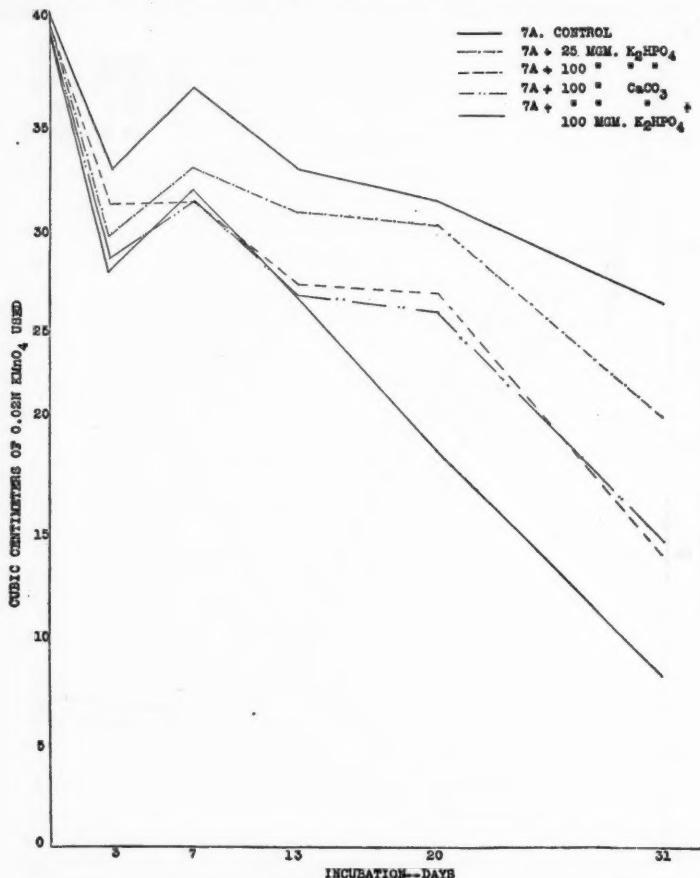


FIG. 3. INFLUENCE OF ADDITION OF SOLUBLE PHOSPHATE AND LIME TO AN INFERTILE ACID SOIL UPON ITS MANNITE-DECOMPOSING POWER

This question is further illustrated in table 8, where the results are presented of a study of the influence of soil treatment upon its mannite decomposing power and of the addition of phosphate or lime or both to a fertile soil (5A), not requiring any phosphate, and to an infertile soil (7A), greatly in need of available phosphate.

The most active mannite-decomposing soils were again those that have received minerals and manure; these were followed closely by the limed plot (7B) and the limed plot receiving minerals, lime and ammonium sulfate (11B). In other words, the limed plots are more active in decomposing mannite than the unlimed plots. The manured soils are leading both among the limed and unlimed, especially so in the unlimed soils. A definite correlation between the mannite-decomposing power and the crop yield for 1923, is thus obtained:

Mannite-decomposing power (decreasing order): 5A, 9A, 11A, 7A; 5B, 11B, 7B

Crop-producing power (decreasing order): 5A, 9A, 11A, 7A; 5B, 11B, 7B

The addition of phosphate as well as lime or lime and phosphate did not increase the mannite-decomposing power of 5A, showing that this soil does not need any available phosphate; the addition of phosphate or lime, and especially lime and phosphate together, to the unfertile soil 7A greatly increased its mannite-decomposing power; the addition of phosphate and lime to the most unfertile soil resulted in almost as high a mannite decomposing power as that found for the fertile soils. This is clearly brought out in figures 1, 2, and 3.

#### SUMMARY

The ability of a soil to fix nitrogen, when an excess of a readily available source of energy is added to it, depends upon the microbial flora of the soil, the physico-chemical condition of the soil, especially its reaction, and upon the presence of available phosphates and potassium salts.

It was found, as a result of the previous studies on the microbiological condition of the soil that the determination of numbers of microorganisms in the soil, nitrifying capacity,  $\text{CO}_2$ -producing capacity and cellulose-decomposing capacity help us to get an insight into the microbiological condition of the soil. The first tells us about numbers of different groups of microorganisms as affected by soil treatment; the second deals chiefly with the rapidity with which the soil nitrogen can become available; the third with the rapidity of decomposition of the soil organic matter and the fourth with the total available nitrogen in the soil. Next to nitrogen, the most important element in the nutrition of plants is phosphorus. None of the above four methods gives a direct indication as to the amount of available phosphorus in the soil. This can be done by the method discussed in this paper, namely by measuring the nitrogen-fixing or mannite decomposing power of the soil.

The determination of the nitrogen-fixing capacity of the soil, as a result of addition of mannite to the soil, is unreliable, due to the small amounts of nitrogen fixed and to the non-sensitiveness of the method for determining the total nitrogen in the soil. A study of the disappearance of mannite in the soil by the method suggested by Christensen is much more applicable.

Three methods can, therefore, be recommended for the determination of the nitrogen-fixing and mannite-decomposing power of a soil, with a view of obtaining information on the microbiological flora capable of fixing nitrogen and on the available phosphorus in the soil:

1. The common solution method, consisting in adding 1 or 5 gm. of soil to a standard mannite solution, incubating for 7 to 28 days, then determining the increase in total nitrogen above the control. This serves as an index of the nitrogen-fixing flora of the soil and to some extent of the microbiological condition of the soil.

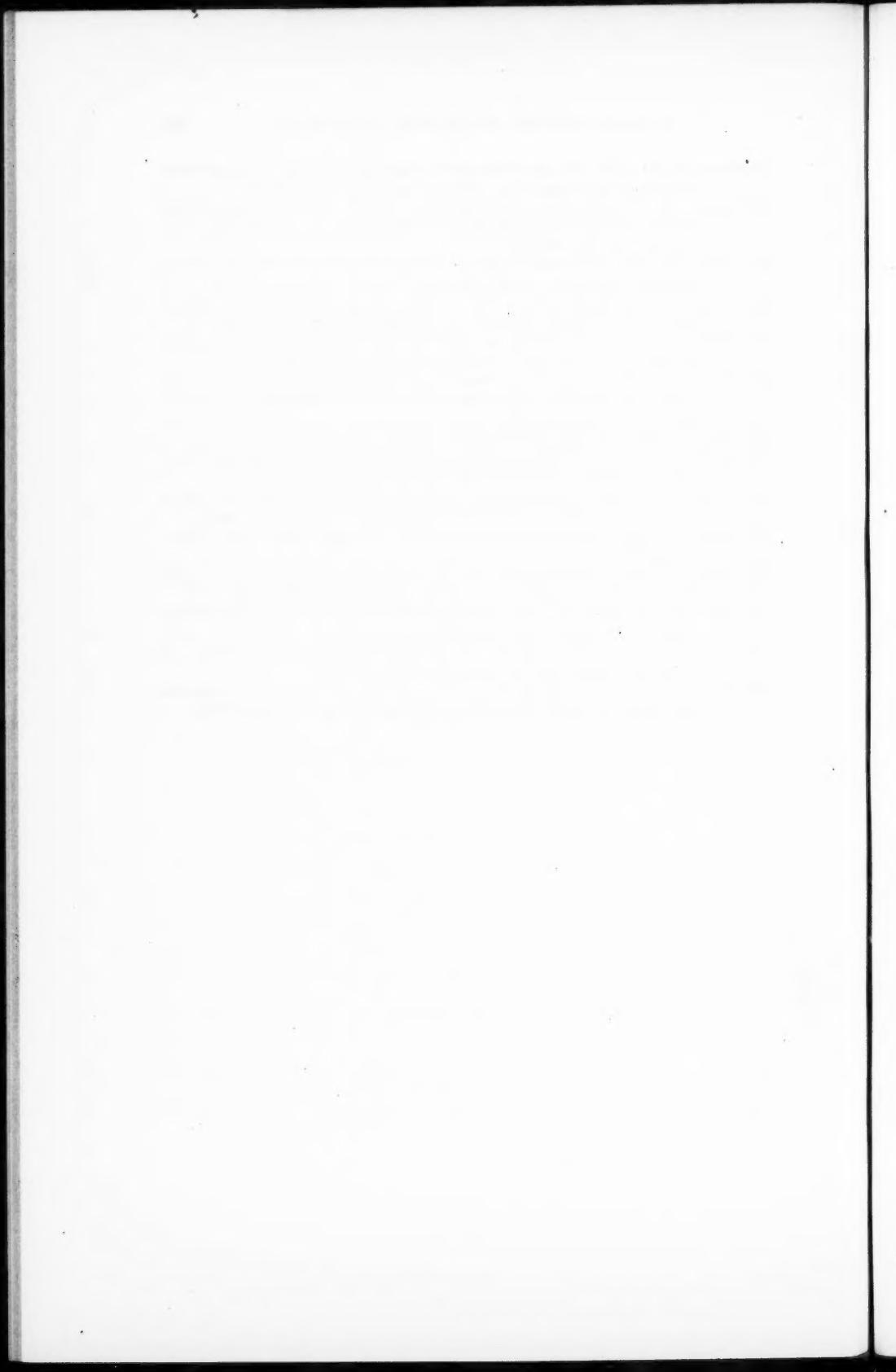
2. The method suggested by Niklewski (18) and Stoklaska (23). This consists in adding 10 gm. of the particular soil to 100 cc. of 2 per cent mannite solution, free from available phosphates, sterilizing and inoculating with a vigorous culture of Azotobacter. After incubating for 20-30 days, the increase in total nitrogen is determined. This can serve as an index of the available phosphate in the soil.

3. The method for determining residual mannite (or rather soluble organic matter in the soil) suggested by Christensen (8). This consists in adding 2 per cent of mannite to the soil, incubating with optimum moisture, then determining the residual mannite, every five days, by oxidation with  $KMnO_4$ . This method as well can serve as an index of the activities of the nitrogen fixing flora and of the amount of phosphorus available in the soil.

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## ALKALI SOIL INVESTIGATIONS: I. A CONSIDERATION OF SOME COLLOIDAL PHENOMENA<sup>1</sup>

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Most of the work on alkali soils has been directed toward a solution of the problems of removing the excess of alkali from the soils or neutralizing the harmful effects of these salts as by converting the black alkali into white and leaching out or scraping off from the surface the accumulated salts. Attempts have been made to determine the mode of formation of alkali soils, also the possible reactions involved when the soils are treated. Most attention, however, has been given to the study of the tolerance of various plants to concentrations of salts comparable to those found in alkali soils. In recent years some of the experiment stations, notably the California Station and some European investigators, especially in Russia, began a series of studies with the hope of revealing the nature and origin of the alkali soils and the reactions involved. It was recognized that a thorough understanding of these factors was necessary before any rational methods of treatments could be followed. One of the most important features of the recent investigations is the appreciation of the colloidal nature of some of the phenomena accompanying alkali soils.

In the course of an investigation conducted at the New Jersey station by the authors following up the suggestion of Lipman (12) to utilize the biochemical oxidation of sulfur for the amelioration of alkali soils the problem of the colloids has been considered. It was felt that a consideration of the alkali problem would be otherwise incomplete. Before we analyze the colloids in question it is necessary to review the general ideas on the subject of colloids within the realm of reactions directly related to those which may be manifested and demonstrated in the complex colloidal system of the alkali soils.

Gedroiz (5) discusses this problem. He states "The moist soil represents a dispersed system in which the soil solution is the dispersed medium and the soil organic and mineral particles are the dispersed phase. Such a system depending on the mechanical composition of the soil (degree of dispersion of the soil particles) possesses surface energy of varying degrees. Phenomena which take place in a dispersed system are subject to the fundamental law of colloid chemistry which states: 'Each dispersed system tends to decrease its free surface energy.' Since the surface energy equals the product of the total surface of the

<sup>1</sup> Paper No. 175 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

<sup>2</sup> The authors share equal responsibility and credit for the work reported.

dispersed phase and the surface tension at the point of contact of the particles of this phase and the dispersed medium, the tendency of the system to decrease its surface energy consists in an effort to decrease the size of the total surface, e.g. decrease the degree of dispersion and the amount of surface tension of the dispersed medium. In the case of soils the latter applies to the soil solution. . . . There are substances which will decrease the surface tension of water, for example acetic acid or most of the organic acids and bases, substances of high molecular structure, (like the alkaloids and dyes). There are also substances which will increase the surface tension, such as inorganic salts, acids and bases and organic substances with a high hydroxyl content, like sugars. These substances, however increase the surface tension in rather less degree than those that decrease the surface tension. The effort of the dispersed system to decrease the surface tension as outlined may be accomplished by the change in concentration of the substances in that layer of the dispersed medium which is indirectly adjoining the surface of the dispersed particles; if with the increase in the concentration of a dissolved substance, the surface tension of the water is de-

TABLE 1

*Surface tension of extracts of treated and untreated alkali soils at various incubation periods*

| SULFUR TREATMENT<br>PER ACRE | SURFACE TENSION AT  |                     |                       |
|------------------------------|---------------------|---------------------|-----------------------|
|                              | 22°C. after 15 days | 19°C. after 75 days | 19°C. after 190 days* |
| pounds                       | dynes               | dynes               | dynes                 |
| None                         | 63                  |                     |                       |
| None                         | 69                  | 71.0                | 71.0                  |
| 2,000 S                      | 73                  | 72.42               |                       |
| 2,000 T                      | 73                  |                     |                       |
| 4,000 S                      | 73                  |                     | 73.13                 |
| 4,000 T                      |                     | 72.42               |                       |
| 6,000 S                      | 73                  | 74.5                | 74.5                  |
| 6,000 T                      | 72.3                | 74.5                | 74.5                  |
| 4,000 c.p. alum              | 71.58               |                     | 73.8                  |

S = Sulfur applied to surface 4 inches.

T = Sulfur mixed with bulk of soil.

\*These extracts were made up from unleached soils; all others were from leached soils. The cultures from this series were incubated at room temperature. They consisted of 3 pounds of alkali soil with the various treatments in earthenware glazed pots, one quart capacity with holes on the bottom to facilitate leaching. A detailed description will be found in a subsequent publication.

creased, then on account of the efforts of the system—soil + solution of such substance—to decrease the surface tension, the substance in question (let us say, acetic acid) will concentrate in the layer of water at the surface of the particles. This is spoken of as adsorption on the surface of the soil particles. The solution of such a substance mixed with soil will be heterogenous at various places in the system; if we consider two neighboring soil particles, we find that at the surface of the particles we have the most concentrated solution and as we move away from the particles approaching their mean center the concentration of the solution is lowering. The phenomenon of the increased concentration of a dissolved substance in a layer of the dispersed medium indirectly adjoining the particles of the dispersed phase is known as *positive adsorption*. Substances which increase the surface tension of the dispersed medium cause the reverse phenomenon—*negative adsorption*; solutions of such substances with the increase in concentration increase the surface tension; the effort of the dispersed system to decrease the surface energy is accomplished

through a lowering in concentration of the dissolved substance in the layer of the dispersed medium adjoining the particles. Thus with substances of the first group (which decrease the surface tension) the dispersed phase attracts to its surface from the dispersed medium the dissolved substances (positive adsorption); with substances of the second group (which increase the surface tension) repulsion of the dissolved substances takes place (negative adsorption)."

The above considerations are supported by the well known theorem of Gibbs in the thermodynamic consideration of adsorption phenomena, and may be summed up in the citation of Lewis (12, p. 304).

"Gibbs showed, as a thermodynamical necessity, that if a dissolved substance had the property of lowering the surface tension of the solution the substance would exist at a higher concentration in the surface layer than in the bulk of the solution."<sup>3</sup> The theoretical considerations of Gibbs' theorem have a bearing on the physical adsorption of the soil particles. Positive adsorption protects the soil from leaching out the easily soluble substances. On the other hand negative adsorption has the reverse influence. In the alkali soils the reduction of positive adsorption and increase of negative adsorption is of prime importance. One of the problems of reclamation of alkali soils is the washing out of the soluble salts. This is facilitated by a decrease of the positive adsorption. This may be accomplished by decreasing the size of the total surface of the dispersed phase. The coagulation of the colloids is therefore a step in this direction. The soils where coagulation took place the capillary rise of the water increased as shown later, the permeability also increased, the surface tension of the soil extracts increased, thus favoring negative adsorption.

Table 1 gives the data on the surface tension of the alkali soil extracts.

In general it is known that suspensoids hardly alter the surface tension; on the other hand colloid solutions increase or decrease the surface tension depending on the colloid. According to Ostwald (16) gum arabic or starch increase the surface tension of water while gelatin, glue, egg-albumin decrease. The data in table 1 show that the colloids in the alkali soil extract decrease the surface tension;<sup>4</sup> this increases positive adsorption and prevents the leaching of alkali soils; on the other hand the oxidation of sulfur increased the surface tension most and thus increased negative adsorption which is favorable for leaching. The alum treatment also increased the surface tension but in less degree than the products of sulfur oxidation. As a result of the change in surface tension and decrease of the total surface of the dispersed phase the negative adsorption is tremendously increased. The physical condition thus changed,

<sup>3</sup> Those interested in a more detailed discussion of this theorem will find helpful the mathematical expression of Gibb's theorem:

$$\Gamma = - \frac{c}{RT} \cdot \frac{d\sigma}{dc}$$

where  $\Gamma$  equals the excess of the dissolved substance in the dispersed medium per unit surface of the dispersed phase as compared with what would have been in the absence of this surface;  $c$  = concentration of the dissolved substance in the dispersed medium;  $T$  = absolute temperature;  $R$  = the gas constant;  $\sigma$  = surface tension;  $\frac{d\sigma}{dc}$  = the differential, expressing increase or decrease of surface tension with the increase of concentration of the dissolved substance. The deduction of this equation was made by Freundlich (see Lewis 12, p. 305).

<sup>4</sup> The apparatus used for the surface tension determinations was that of du Nouy (15).

causes greater permeability and allows the leaching of soluble salts. The expression of this phenomenon may be found in the rate of leaching or in the rise of capillary water. Figures 1 and 2 give the curves of a series of soils treated as outlined in table 2. These two sets of curves represent two different incubation periods,<sup>5</sup>—one after 14 days, the other after 95 days. It will be noted that after 14 days the differences in capillary rise are not great. All cultures showed practically the same rate of rise of water. The cultures treated with alum have total rise greater than any other. This indicates that the strongly adsorbed trivalent aluminum ion exerted its influence by coagulating the colloids and thereby decreasing the surface. As we turn our attention to figure 2 an entirely different picture presents itself; the outstanding fact is the rise of the capillary water in the cultures treated with sulfur. On the other hand, the curve for the culture treated with alum no. 8, runs alongside the

TABLE 2  
*Treatment of alkali soils and the rate of leaching after 95 days incubation*

| LABORATORY NUMBER OF CULTURE | TREATMENT PER ACRE                                | AMOUNT LEACHED AFTER |          |
|------------------------------|---|----------------------|----------|
|                              |   | 7 hours              | 48 hours |
| 1                            | None.....   | 40                   | 75       |
| 2                            | 4000 pounds sulfur.....                           | 97                   | 285      |
| 3                            | 4,000 pounds sulfur + 5 tons peat.....            | 190                  | 298      |
| 4                            | 6,000 pounds sulfur.....                          | 197                  | 290      |
| 5                            | 6,000 pounds sulfur + 5 tons peat.....            | 167                  | 293      |
| 6                            | 2,000 pounds sulfur.....                          | 42                   | 90       |
| 7                            | 2,000 pounds sulfur + 5 tons peat.....            | 68                   | 150      |
| 8                            | 4,000 pounds c.p. alum + 5 tons peat .....        | 44                   | 138      |
| 9                            | 4,000 pounds c.p. alum + 2,000 pounds sulfur..... | 80                   | 210      |
| 11                           | 5 tons peat.....                                  | 00                   | 53       |

untreated or the peat culture. The effect which was apparent after 14 days of incubation gradually disappeared upon further incubation. This is very significant and the discussion of such behavior of the alum will be found later when the coagulation of colloids is taken up. The same may be said about culture 9 which is manifesting the effects of the combined alum and sulfur treatment. In general it is evident that the cultures treated with sulfur have undergone pronounced surface influences allowing greater permeability and therefore a greater rise of the capillary moisture. Table 2 gives some figures on the rate of leachings. While the phenomenon of capillary rise of moisture is an indirect criterion for the change of surface due to the coagulation of the colloids and change in surface tension the data on the leaching are a direct criterion. The data on the rate of leaching after 95 days is very typical for all the series of experiments which will be reported presently. The soils treated with sulfur

<sup>5</sup> The whole series of capillary studies will be reported in the paper following.

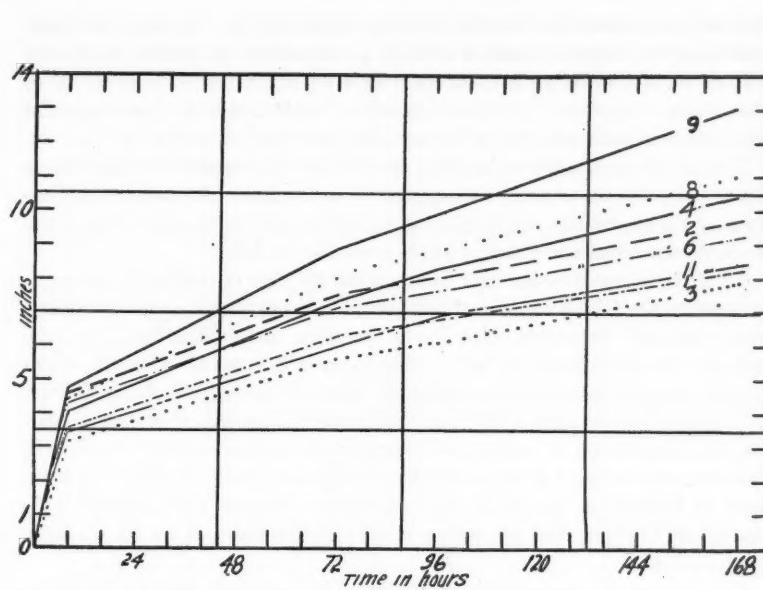


FIG. 1. CURVES SHOWING RISE OF CAPILLARY WATER IN FIRST SERIES AFTER 14 DAYS' INCUBATION

Numbers indicate treatment as outlined in table 2

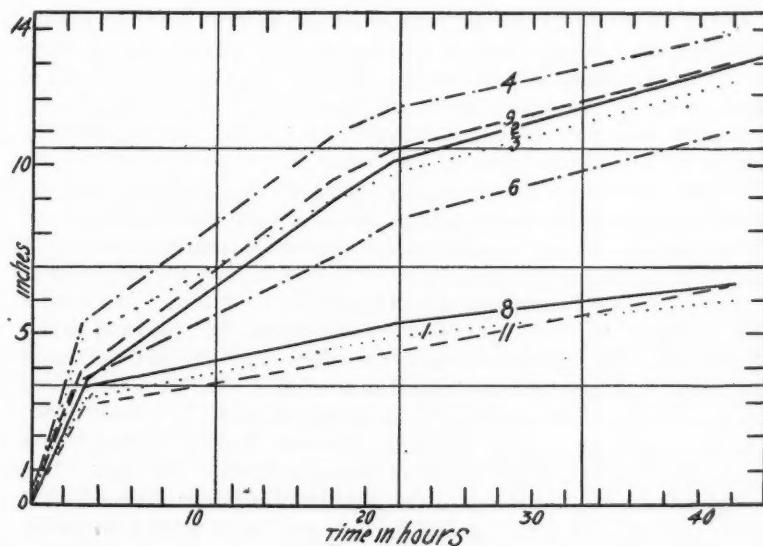


FIG. 2. CURVES SHOWING RISE OF CAPILLARY WATER IN FIRST SERIES AFTER 95 DAYS' INCUBATION

became most permeable to water, allowing rapid leaching. In many instances even after 6-7 days of contact culture 1, untreated, or culture 8 treated with alum, had water on the surface. This water was either poured off or allowed to evaporate. Attention must be called again to the beneficial effects of the treatment with sulfur and alum combined, in culture 9.

The cultures subjected to leaching consisted of 1.4 pounds of alkali soils in flower pots; 400 cc. of water was applied to the surface. A more detailed account of the experiment will be given in the subsequent papers where the analyses of the leachings and extracts will be presented in full.

All of these considerations are based on the theorem of Gibbs, but we must remember that Gibb's expression in its entirety is applicable under conditions where chemical effects and solubility of the solute in the adsorbing phase are reduced to a minimum (11, p. 305). This is true in the case of charcoal. However, it is doubtful whether the chemical effects of the soil solution in contact with the soil particles are negligible. This must be borne in mind in considering the phenomenon of positive and negative adsorption in soils. In general, however, the forces of physico-chemical adsorption based on Gibb's theorem must be accepted as playing an important part. The work of Langmuir (11) also seems to show that adsorption may be looked upon as purely chemical phenomenon.

Coming back to the coagulation of the colloids we shall consider the forces which tend to accomplish this desirable process in alkali soils.

#### COAGULATION OF COLLOIDS

One of the important generalizations of colloid chemistry is the one dealing with the coagulation of colloids by electrolytes. This generalization is known as the Hardy-Schulze Law and reads as follows: "Ions carrying a charge of sign opposite to that carried by the colloid are the most active precipitants, and at the same time the higher the valence of the ion (i.e. the greater the number of unit charges upon it) the greater its precipitating action." If the colloid is positively charged then, of course, the negative ions of high valence are the most effective precipitants, the reverse is true with colloids negatively charged. Besides coagulation by electrolytes, colloids may also be coagulated by heating or cooling the colloidal solution or by electrolysis (more correctly speaking by cataphoresis), the particles being carried in virtue of their charge to one of the electrodes where they become discharged and assume the gel form. The adsorption of cations or anions (depending on the charge of the colloid) is of importance in coagulation of colloids. The lower the valence the more it is adsorbed, although it is not always the case. In a recent paper, Chatterji and Dhar (2) show that pure manganese dioxide will adsorb 0.0015 equivalents of silver but only 0.00033 of barium or 0.0001 of aluminum. This would indicate that the charge is the determinative factor. In speaking of coagulation we must remember that the hydrogen ions of acids, even though

monovalent, have a coagulation power equal and sometimes greater than that of divalent or even trivalent metals. This fact should be kept in mind as we shall see the effect of coagulation power of the hydrogen ions of the sulfuric acid formed by the biochemical oxidation of sulfur in alkali soils. The hydrogen ion introduced into a dispersoid is of extreme importance in the coagulation of colloids as we shall see presently.

TABLE 3  
*Effect of alum, sulfuric acid or a combination on the coagulation of colloids in alkali soil extract*

| TUBE NUMBER | TREATMENT       |  |                | REACTION OF SUPER-NATANT LIQUID | RELATIVE AMOUNT OF COAGULATION                      | INTENSITY OF COLOR IN SUPER-NATANT LIQUID |
|-------------|-----------------|--|----------------|---------------------------------|---|---|
|             | 0.01 M alum cc. | 0.1 M H <sub>2</sub> SO <sub>4</sub> cc. | 1.0 M NaOH cc. |                                 |   |   |
| 1           | 1               |  | 0.8            | 9.0*                            | Considerable  | Slight                                    |
| 2           | 1               |  | 1.0            | 9.2*                            | Very slight after 24 hours                          | No apparent change                        |
| 3           | 1               |  | 1.1            | 9.3*                            | None  | No apparent change                        |
| 4           | 1               |  | 2.0            | 9.6*                            | None  | No apparent change                        |
| 5           | 1               |  |                | 4.8                             | Practically instantaneous                           | Clear as water                            |
| 6           | 0.5             |  |                | 6.0                             | Heavy   | Very slight                               |
| 7           | 0.3             |  |                | 7.0                             | Heavy   | Very slight                               |
| 8           | 0.2             |  |                | 7.0                             | Appreciable   | Slight                                    |
| 9           | 0.1             |  |                | 7.4                             | Slight turbidity; slight precipitate after 24 hours | No apparent change                        |
| 10          |                 | 2  |                | 3.0                             | 1†  | 8†  |
| 11          |                 | 3  |                | 2.8                             | 2   | 5   |
| 12          |                 | 4  |                | 2.6                             | 3   | 4   |
| 13          |                 | 5  |                | 2.4                             | 4   | 3   |
| 14          |                 | 7  |                | 2.0                             | 6   | 2   |
| 15          |                 | 8  |                | 2.0                             | 7   | 1   |
| 16          | 0.05            | 1  |                | 6.0                             | 0   | 10  |
| 17          | 0.1             | 2  |                | 3.0                             | 3   | 4   |
| 18          | 0.15            | 3  |                | 2.6                             | 7   | 2   |
| 19          | 0.2             | 4  |                | 2.4                             | 9   | 1   |
| 20          |                 |  |                | 9.2                             | 0   | 10  |

\* The potentiometer was used for these readings.

† The intensities of coagulation and color for tubes 10-20 are indicated by numerical values expressing comparison with the control, tube 20.

Experiments were conducted to ascertain the coagulating effect of sulfuric acid and alum respectively on the colloids of alkali soil extracts. At the same time the reaction at which coagulation takes place was also investigated. For that purpose 25-cc. portions of untreated alkali soil extract were placed in test tubes and various additions of sulfuric acid and alum solutions were added. Table 3 gives the plan and results of the experiments.

It will be noted that the alum treatment is most efficient in coagulating the colloids. However, not until the reaction reaches pH 7.4 does the alum begin to show its coagulating power. At pH 7.0 we get heavy coagulation, although the rate of coagulation is delayed. That not all the colloids have been precipi-

itated may be judged from the persistence of some color in the supernatant liquid. It is remarkable that at pH 4.8 (tube no. 5) the rate of coagulation was practically instantaneous. This would suggest that it is the isoelectric point at which any colloid is most unstable as pointed out by Hardy (7, 8). In this connection it is appropriate to recall the work of Loeb (14) who shows that the isoelectric point of gelatin is at pH 4.7. In tube 1 with the pH 9.0 there was only some coagulation even though the amount of alum added was the same as in tube 2. This would indicate that the reaction has some effect on the coagulating power of any substance. On the other hand, tube 3 shows that at pH 9.2 and above the alum has no coagulating power. Of course we must remember that in these cases the presence of the peptizing agent is of prime importance in the stability of sols. It has been shown recently by Thomas and Johnson (18, 19) that precipitation (coagulation in our case) is due to removal of peptizing agents by chemical action between them. In our case the addition of the NaOH means an increase in the peptizing agent and thus stability of the colloid sols. From the data on the combination of alum and sulfuric acid it seems as though the reaction plays no important rôle in the coagulation of the colloids in this particular case; tube 16 with a pH reading of 6.0 showed no effects even after a prolonged standing of seven days. At the same time, tube 6 showed heavy coagulation immediately after addition of the alum. Unquestionably the trivalent aluminum ion is responsible for the coagulation effect, whether by ionic neutralization of electric charges, by selective adsorption, or both. Of extreme interest is the combined effect of the alum and sulfuric acid. Taking tubes 9 and 17 and comparing the effects we note that no. 17 had appreciable coagulation and the color intensity changed markedly; on the other hand no. 9 had only very slight coagulation and no apparent change in coloration. Still the amount of alum added was the same in both cases. Tubes 19 and 8 are comparable in the same sense. The differences may be due to the hydrogen-ion concentration variant; this explanation may find its support in some of the figures as pointed out. It is more likely, however, that we have here an entirely different phenomenon. In dealing with coagulation effects we must consider both the cations and anions and more so the mutual effect of two cations or anions. By adding  $H_2SO_4$  and alum we do not modify the anion effect of the alum, since both anions are the same, but we introduce a different cation. If one cation has a coagulation power equal to  $x$  and another the coagulation power equal to  $y$ , the combined cations have not a coagulation power equal to their algebraic sum  $x + y$ . Generally the combined effect is greater than the sum. The increase is not in an arithmetic progression. Such an effect could be noticed in the combined effects of alum and sulfuric acid. The curves on the capillary rise in figures 1 and 2 prove the same thing.

From what has been said it is logical to conclude that in the coagulation of colloids the quantitative relationships of the colloids precipitated should follow the same tendency, namely that with alum and sulfuric acid more of the col-

loids should be precipitated than with either ingredient singly. With this in view 50-cc. portions of alkali soil extract from untreated soils were taken and treated in the manner given in table 4. It is significant that the precipitate of tube 5 carried more iron and silica than any other treatment. Undoubtedly we have here the combined effect of the aluminum and hydrogen-ion. It is also worth while to note the reaction at which most of the colloids precipitate. Again the probable isoelectric point played its part. These experiments were repeated with variously treated soils and the results were very similar. We need not go into a more detailed discussion of this complicated subject; for our purpose it will suffice to accept with reservation the law of Hardy and Schulze in relation to coagulation.<sup>6</sup> It is known that the colloids in soils are negatively charged although there is the possibility of a high iron and aluminum colloidal sol content which are positive. In order to prove that the colloids in the alkali soil extract (untreated) are negatively charged the routine experiments in colloid chemistry for the determination of the charge was

TABLE 4  
*Effect of alum and sulfuric acid on colloids precipitated*

| NUMBER OF TUBE | TREATMENT   |                                      | REACTION | KMnO <sub>4</sub> FOR Fe TITRATION | SiO <sub>2</sub> |
|----------------|-------------|--------------------------------------|----------|------------------------------------|------------------|
|                | 0.01 M alum | 0.1 M H <sub>2</sub> SO <sub>4</sub> |          |                                    |                  |
| 1              | 2           | cc.                                  | 4.7      | 1.25                               | 1.0              |
| 2              |             | 2                                    | 8.4      | *                                  | *                |
| 3              | 1           | 1                                    | 6.4      | 1.25                               | 0.8              |
| 4              | 0.5         | 1.5                                  | 7.4      | 0.9                                | 0.9              |
| 5              | 1.5         | 0.5                                  | 4.8      | 1.80                               | 1.5              |

\*No precipitate was formed.

carried out. The procedure was as follows: An arsenic trisulfide sol was prepared by mixing equal volumes of a 1 per cent arsenous acid solution (dissolved by boiling and filtered cold) and distilled water saturated with H<sub>2</sub>S. The mixture was boiled for over one-half of an hour to drive off the excess of the H<sub>2</sub>S. An iron oxide sol was prepared by pouring 5 cc. of a concentrated ferric chloride solution into 500 cc. of boiling water and continuing to boil for a few minutes. The colloidal solution was then poured into collodion bags and dialyzed in distilled water until practically none of the peptizing agent could be detected in the distilled water. The alkali soil extract was made up by mixing 50 gm. of soil in 500 cc. of distilled water, shaken for several hours and left over night undisturbed. The supernatant liquid was decanted and centrifuged for 1.5 hours at high speed (1000 revolutions per minute). The clear liquid was

<sup>6</sup> The authors are aware of the remarkable researches of Loeb as summarized by him (14). It matters little whether the effects are viewed in the light of stoichiometric considerations as Loeb suggests, or from the viewpoint of Freundlich's and others adsorption theories.

then ready for use; 80 cc. of arsenic trisulfide and iron oxide sols were poured separately into 100 cc. graduated cylinders and to them 20 cc. of the alkali soil extract was added. The mixture was shaken and allowed to be undisturbed. The iron oxide sol after 10-15 minutes began to settle while the arsenic trisulfide sol did not settle at all even after 10 days. This is sufficient proof to show that the alkali soil extract colloids are negatively charged, since the arsenic trisulfide being also negatively charged had no effect. On the other hand the positively charged iron oxide sol caused coagulation. In this connection it is worth while to mention the work of Gordon and Starkey (6) who claim that adsorption of soils is influenced more by iron and alumina colloids than by silica colloids. This may indicate that the chief colloids are iron and alumina and these as a rule are positively charged. This is contrary to the general idea of the charge on soil colloids. There can be no question about the charge of the colloids in alkali soils as shown above.

What then, are the effects of these colloids on the soil properties and how are they modified by coagulation?

In soils the chief colloids are of silica, iron, aluminum, clay and organic materials. The silica colloids are negatively charged and are resistant to precipitants; even metals of high valence have but little effect on their precipitation in soil. This has been pointed out by Ehrenberg (3) and others. The failure of Gordon and Starkey to get adsorption by silica colloids may be due to this property of the silica colloids. This is important inasmuch as in the alkali soil extract silica colloids are quite in abundance and have a protective effect on the other colloids as will be shown presently.

The colloids of the organic substances are known as humus colloids. These colloids are also negatively charged and in alkali soils they exist in the hydro-sol form due to the peptization of the organic matter, the peptizing agent being the sodium carbonate.<sup>7</sup> These colloids perhaps also have a protective effect on the other colloids. The dark brown color of alkali soil leachings is due to the humus colloids. This color is changed upon coagulation with the sulfuric acid formed from the sulfur oxidized; it becomes a pale straw colored liquid.

The hydrated iron oxide colloids are present in soils in greater or smaller degree depending on amount of iron present in the soil; this in turn is influenced by the native minerals. In the alkali soil they are invariably present. The charge of this colloid is positive. The coagulation may be accomplished by the negatively charged anions and also by the negatively charged colloids: This latter subject of mutual precipitation will be dealt with later.

The hydroxide of aluminum is undoubtedly present and behaves somewhat similar to the iron. The clays are degradation products of the silicates and are formed just as the hydrated iron oxide colloids by the hydrolysis of water soluble salts. Clays behave both like an electro-negative and electro-positive

<sup>7</sup> As the oxidation of sulfur progresses and carbonates disappear the peptization of organic matter cannot take place. As the organic colloids are coagulated they do not appear in the leachings and serve as buffers.

colloid depending on conditions. It is possible that the electro-negative behavior of clays is due to protective effects, although a reverse in charge of colloids is not uncommon. Biltz (1) succeeded in coagulating clay with the electro-negative silicic acid colloid. And besides the hydrogen-ion concentration of the dispersed medium has an effect on the charge.

It would lead us too far if we should go into a discussion of the possible reactions due to the colloids. We shall confine ourselves within a limited range of phenomena which manifest themselves in the alkali soils.

It has already been pointed out that any colloid system tends to decrease its free surface energy and this may be accomplished by decreasing the surface tension and by decreasing the total surface. This is determined in a great measure by the size of the dispersed phase. Now the surface of any soil has an effect on the rate of evaporation, since the latter is essentially a surface phenomenon. In soils with a high colloid content the decrease of the dispersed phase will decrease the surface and thus reduce the rate of evaporation, as the latter is more rapid the larger the surface. Keen (9) has shown that, since the vapor pressure influences greatly the rate of evaporation, the colloidal properties of the soil having in turn an effect on the rate of evaporation (due to increase of surface) will thus influence the vapor pressure. In alkali soils with its high colloidal content the coagulation of the colloids decreases its surface and thus should decrease evaporation.

Experiments to ascertain the rate of evaporation as effected by the vapor pressure are complicated in nature and due to the lack of facilities such experiments could not be carried out as planned. Evaporation experiments carried out as shown presently were not satisfactory, still there were indications pointing toward a greater evaporation from the *surface* of soils where the degree of dispersion, as in the case of non-treated soils, is great. On the other hand with the coagulation of the colloids and thus a lowering of the degree of dispersion, as in the case of the soils treated with sulfur or alum, the evaporation is slower from the surface.

Beakers of uniform size were selected, 50 gm. of the alkali soils of treatments as previously described were placed in them and weighed. After 10 cc. of water was added to each, the beakers were again weighed; after 24 hours they were weighed again and loss compensated. After that the beakers were weighed at intervals of time, 5 hours, 18 hours, 24 hours and 42 hours. The reason for allowing the soils to be in contact with water for 24 hours previous to taking the readings was to give the soil a chance to come to its normal condition inasmuch as the drying has an effect on the condition of the colloids going from sol to gel state and vice versa.

It is worth while to record that evaporation from unleached soils was always greatest in the untreated soils in the earlier periods, e.g. after 3, 4, 6 hours. After a more prolonged period evaporation was faster from the treated soils. The changes produced in the dispersoid of the soil due to the various treatments affected the amount of surface and probably also the vapor pressure of the

soil solution. Extracts from the soils as shown in table 5 show very little depression of the freezing point and thus also of the vapor pressure. The latter was determined by calculating the molar concentration in the extracts from the freezing point depression. Then the well known formula of Raoult  $\frac{P - P_1}{P} = \frac{n}{N}$  was applied.  $P$  = the vapor pressure of the solvent,  $P_1$  = the

TABLE 5  
*Lowering of freezing point and vapor pressure of alkali soil extracts at various incubation periods*

| Treatment per acre   | FIRST SERIES            |                 |                         |                | Treatment per acre              | SECOND SERIES |         |          |         |  |
|----------------------|-------------------------|-----------------|-------------------------|----------------|---------------------------------|---------------|---------|----------|---------|--|
|                      | 14 days                 |                 | 140 days                |                |                                 | 75 days†      |         | 190 days |         |  |
|                      | Freezing point lowering | Vapor* pressure | Freezing point lowering | Vapor pressure |                                 | °C.           | mm. Hg  | °C.      | mm. Hg  |  |
| None                 | 0.065                   | 17.352          | 0.05                    | 17.3545        | None                            | 0.042         | 17.3559 | 0.06     | 17.3528 |  |
| 4,000 lbs. S         | 0.067                   | 17.3517         | 0.06                    | 17.3528        | 2,000 lbs. S‡                   | 0.02          | 17.3596 |          |         |  |
| 4,000 lbs. S§        | 0.062                   | 17.3525         | 0.072                   | 17.3508        | 2,000 lbs. S§                   |               |         | 0.052    | 17.3542 |  |
| 5 tons peat }        |                         |                 |                         |                |                                 |               |         |          |         |  |
| 6,000 lbs. S         | 0.062                   | 17.3525         | 0.048                   | 17.3549        | 4,000 lbs. S‡                   |               |         | 0.052    | 17.3542 |  |
| 6,000 lbs. S§        | 0.064                   | 17.3522         | 0.062                   | 17.3525        | 4,000 lbs. S§                   | 0.022         | 17.3592 |          |         |  |
| 5 tons peat }        |                         |                 |                         |                |                                 |               |         |          |         |  |
| 2,000 lbs. S         | 0.062                   | 17.3525         | 0.067                   | 17.3517        | 6,000 lbs. S‡                   | 0.002         | 17.3626 | 0.067    | 17.3517 |  |
| 2,000 lbs. S§        | 0.062                   | 17.3525         | 0.043                   | 17.3557        | 6,000 lbs. S§                   | 0.016         | 17.3603 | 0.074    | 17.3505 |  |
| 5 tons peat }        |                         |                 |                         |                |                                 |               |         |          |         |  |
| 4,000 lbs. c.p. alum | 0.067                   | 17.3517         | 0.052                   | 17.3542        | 4,000 lbs. c.p. alum            | 0.01          | 17.3613 | 0.067    | 17.3517 |  |
| 5 tons peat }        |                         |                 |                         |                |                                 |               |         |          |         |  |
| 4,000 lbs. c.p. alum | 0.068                   | 17.3515         | 0.062                   | 17.3525        | Original extract; not incubated |               |         | 0.082    | 17.3491 |  |
| 2,000 lbs. S         |                         |                 |                         |                |                                 |               |         |          |         |  |
| 5 tons peat          | 0.059                   | 17.353          | 0.052                   | 17.3542        |                                 |               |         |          |         |  |

\* Vapor pressure given is at 20°C.; the vapor pressure of water at this temperature is 17.363 mm.

† Extracts were made up from soils previously leached. All others were from unleached soils.

‡ Sulfur was applied to surface 4 inches.

§ Sulfur mixed with bulk of soil.

= vapor pressure of the solute,  $n$  = the number of moles of solute,  $N$  = the number of moles of solvent per liter (for  $H_2O = 55.52$ ). It is significant that the original soil extract depressed the vapor pressure most. The fact that the treated soils allow more intense evaporation after six hours is therefore not due to the vapor pressure, as far as the extract data is concerned, but to other causes. It is very likely that the treatments which change the permeability

and coagulate the colloids also produce better aeration, and that the greater evaporation after six hours is due to that factor.

Another very important consideration in connection with the properties of colloids and their relation to alkali soil treatment is the effect of colloids on the permeability of the soil. The impermeability of alkali soils is a well known condition. When water is applied to alkali soils it does not penetrate the soil for a long time. The capillary rise of the water is also very slow as brought out by the data on capillary studies conducted at the various incubation periods in treated and untreated alkali soils. Kellerman (10) attributes the impermeability of certain Nevada soils to the presence of colloidal silica. The same idea is expressed by Scofield (17). However, it is quite possible that other colloids, especially the organic, play an important part. It may be that the phenomenon of impermeability in alkali soils is similar to that of hard pan and that the colloids serve as a cement at periods of drying out of the soils. The conversion from sol to gel and vice versa at various stages of moisture content will accentuate the condition. At any rate alkali soils have a sponge effect, holding the water after they take it up. The capacity of colloids to hold or absorb large amounts of water is a well known phenomenon in colloidal chemistry. After treatment with a coagulating agent such as alum or sulfuric acid the permeability of the alkali soil is greatly improved. The degree of improvement goes hand in hand with the coagulation of the colloids; the more the colloids are coagulated the better is the permeability.

In normal soils the colloids serve as retentive agents of various constituents, retarding leaching. In alkali soils this colloidal property is, as pointed out, a hindrance reducing permeability, aeration and increasing the retentive power and thus the accumulation of salts after drying.

Mutual coagulation of colloids is well known and is likely to occur in soils which contain side by side the positive iron and aluminum colloids with the negatively charged silica and organic colloids. The recent work of Freundlich and Nathansohn (4) seems to show that even colloids of the same charge precipitate each other. It is also true that the quantitative relationships of the respective colloids have a great deal to do with their mutual coagulation. In the alkali soil extracts we have been able to demonstrate the preponderance of negatively charged colloids and the question arises what becomes of the positively charged iron and aluminum? It is suggested by the authors that there must be some protective effect. The silica or organic colloids, being negatively charged protect the positively charged iron colloids, which are not, however, coagulated by the oppositely charged silica colloids. It is also possible that even the iron and aluminum colloids have changed their charge after going through the isoelectric point. In the experiments to determine the charge in the alkali soil colloids as reported above, the amount of silica colloid coagulated was also determined. It was found that the addition of the positively charged hydrated iron oxide colloid coagulated more than 25 per cent of the silica.

In the next article the origin of alkali soils will be discussed, and data on the methods used for the amelioration of these soils will be presented and critically discussed.

#### SUMMARY

Positive and negative adsorption in the system—soil and soil solution—are of great importance in leaching out soluble substances.

In alkali soils, negative adsorption is desirable.

Coagulation of colloids increases the surface tension of the extract and modifies the physical condition of the alkali soils. These changes are manifested in the capillary rise of water and permeability of soils to water.

The effect of alum and sulfuric acid or both on the coagulation of alkali soil colloids was investigated. The effect of alum and sulfuric acid in combination is greater than that of either one separately. At pH 4.7 coagulation is practically instantaneous, pointing to the possibility of this being the isoelectric point.

The colloids of alkali soils are negatively charged and are precipitated therefore with positively charged colloids, or electrolytes with cations of high valency.

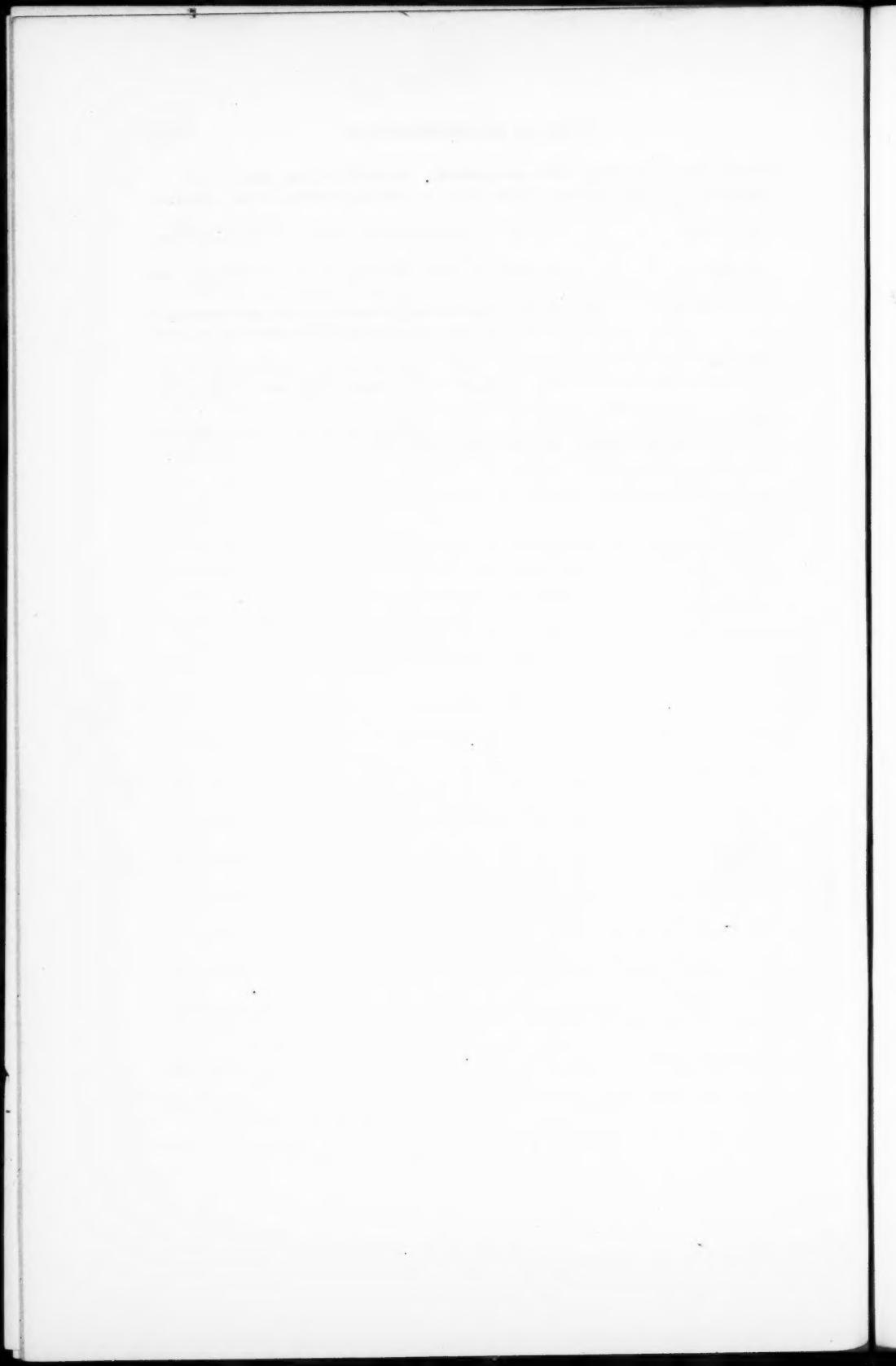
The dispersed phase affecting the surface influences evaporation. The vapor pressure of alkali soil extracts is changed but little due to various treatments.

The nature of the impermeability of alkali soils and the protective effect of colloidal silica and organic colloids are discussed.

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## THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION CONTROL IN PHYSICO-CHEMICAL STUDIES OF HEAVY SOILS

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The extent of the recent literature on the measurement of hydrogen-ion concentration and its application to almost every branch of chemistry is evidence of the importance of hydrogen-ion concentration control (8). It is of especial importance in reactions of weak acids or bases and their salts such as occur in soils. Most of the numerous soil studies, in which the hydrogen-ion concentration has been considered, fall into one of six groups:

1. Studies of the variations in the pH value of natural soils, including the effect of the water content and of drying upon that value.
2. The relation of the hydrogen-ion concentration of soils to plant distribution.
3. The effect of the pH value of the soil upon that of the juices of plants growing on it.
4. The effect of the pH value of the soil upon the microbiological activities in it.
5. Titration curves in which the effect of additions of acids or bases upon the pH value is measured.
6. Studies of the relation of the pH value of the soil to its lime requirement as determined by the numerous lime requirement methods.

In much of the work on the effect of chemical treatments upon the flocculation of soils and upon the absorption and exchange of bases by soils, however, the importance of hydrogen-ion concentration control has not always been fully appreciated. Recent work in this laboratory and elsewhere indicates that the hydrogen-ion concentration existing after the soil and the treatment have reached equilibrium is one of the most important factors in determining the course of the reaction. This paper will treat only this type of investigation.

### FLOCCULATION

The hydrogen-ion has long been known to be an effective flocculant for colloidal clay. The rôle of the hydroxyl ion has not been so clear. Maschhaupt (19) and others have shown that small amounts of an alkali tend to stabilize soil suspensions while larger amounts cause flocculation. Comber (9) found that clay suspensions were flocculated most readily in an alkaline mixture but he did not give its pH value. He estimated the flocculating power of different electrolytes, however, by observing the rate of settling of the coagulum formed by a decided excess of the electrolyte. Numerous observations

in this laboratory (3) as well as those of Smith (25), Arrhenius (1), Burton (7), and others show that the addition of certain electrolytes in excess of the minimum required for flocculation, yields a coagulum that settles more slowly than if just enough is added to flocculate the colloid. This may be the reason for the apparent differences in the results of Comber and Maschhaupt. Tartar and Gailey (31) and Michaelis and Hirabayashi (22) have pointed out the importance of hydrogen-ion concentration control in the flocculation of mastic sols and have shown that many of the so-called "specific effects" attributed to the ion of the same charge as the colloid would disappear if the different electrolytes having the same cation were compared at the same Sörensen value.

The studies made in this laboratory (4) furnish convincing evidence of the necessity of hydrogen-ion concentration control if we are to obtain an adequate conception of the phenomena of flocculation in soils. All of the work reported here has been done on the colloidal fraction of the soils, separated by the method developed in this laboratory (3). These colloidal clay solu-

TABLE 1  
*Results with acids*

| ACID  | MILLIEQUIVALENTS REQUIRED | pH WITH COLLOID | pH WITHOUT COLLOID | DIFFERENCE |
|---|---------------------------|-----------------|--------------------|------------|
| HCl.....  | 0.48±0.02                 | 3.9             | 3.5                | 0.4        |
| H <sub>2</sub> SO <sub>4</sub> .....                    | 0.50±0.02                 | 3.9             | 3.5                | 0.4        |
| H <sub>3</sub> PO <sub>4</sub> (as monobasic acid)..... | 0.73±0.016                | 3.7             | 3.3                | 0.4        |
| H <sub>3</sub> PO <sub>4</sub> (as tribasic acid).....  | 2.20±0.05                 | 3.7             | 3.3                | 0.4        |
| Acetic.....   | 5.5 ±0.5                  | 3.8             | 3.7                | 0.1        |
| Citric.....   | 6.5 ±0.5                  | 3.2             | 3.1                | 0.1        |

tions were comparatively uniform in the size of their particles, ranging between 20 and 80 milli-microns in diameter. They were very stable having but very slight tendency to settle out by gravity alone. Studies on their probable chemical nature indicate that they are composed largely of complex alumino-silicates. The minimum electrolyte requirement was determined by the usual trial and error method, observations being taken twenty-four hours after mixing the electrolyte with the clay. The results with a series of acids as given in table 1 show that while the minimum requirement varies as much as ten-fold if expressed in terms of milliequivalents per liter, or total titrable acidity, ranging from 0.48 of a milliequivalent for hydrochloric acid to 5.5 milliequivalents for acetic acid. All the acids, except perhaps citric, flocculate at approximately the same pH value, which in the case of this acid clay is about 3.8.

A series of mixtures having the same potassium content and varying in pH value between 3 and 13 gave the results plotted in figure 1. Curve 1 was obtained with an acid colloidal clay and curve 2 with a neutral clay. The

values for the acid clay are very significant. The electrolyte requirement increases gradually as the hydrogen-ion concentration decreases until the neutral point is approached then rises very quickly to a constant value. Variations in Sørensen values between about pH 8.5 and pH 12 had no effect whatever upon the minimum electrolyte requirement. Solutions made up of nine parts KCl and one part KOH flocculated at the same concentration of potassium as solutions of KOH alone, although ten times as much KOH was required as with KCl alone. This sudden increase at the neutral point in

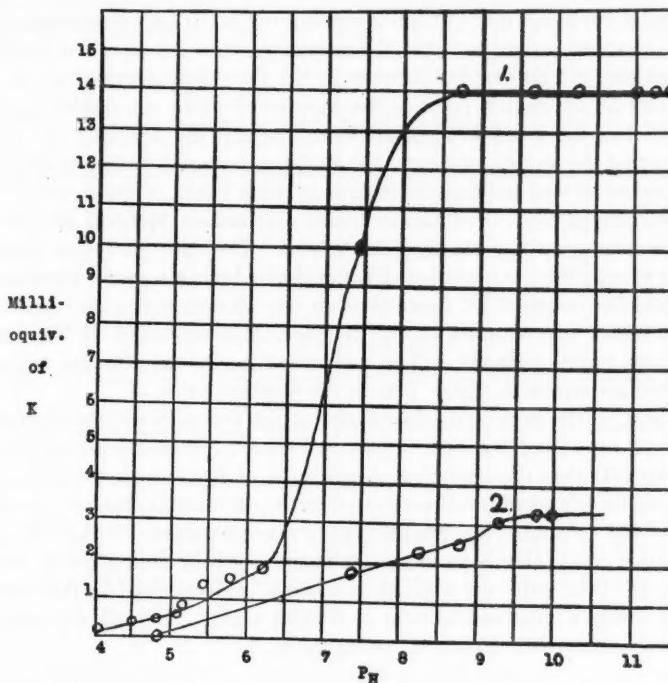


FIG. 1. THE EFFECT OF H-ION CONCENTRATION UPON THE FLOCCULATION OF AN ACID (1.) AND A NEUTRAL (2.) COLLOIDAL CLAY

case of the acid soil indicates that the alkaline mixtures have one function more than the other mixtures. They must neutralize the acid clay, then flocculate the resulting potassium salt of the clay. The acid clay seems to be neutralized before the pH value of 9 is reached, since from that point on further increases in alkalinity are without effect. If the sudden increase in electrolyte requirement near the neutral point in the case of the acid clay is due to the fact that a part of the KOH in the mixtures is used up in converting the acid clay into its potassium salt, a neutral clay should show no marked

change in electrolyte requirement at the neutral point. Curve 2 on figure 1 was obtained with a clay having a pH value of about 7. As would be expected the steep region of the curve is almost entirely lacking. Several other acid and neutral clays were studied and the above curves were found to be typical of their respective classes. The flocculating power of a series of calcium mixtures of varying Sörensen values was found to vary in the same way. The amount of calcium required in each case was, of course, considerably smaller probably because of the greater insolubility of the calcium-aluminosilicates formed.

Comber (9) found that  $\text{CaCl}_2$  was superior to  $\text{Ca}(\text{OH})_2$  for flocculating very dilute clay suspensions but that the reverse was true for more concentrated suspensions. If the sudden increase in the electrolyte requirement of the acid clay at the neutral point in the experiment above was due to the fact that part of the KOH was utilized in neutralizing the acid clay, we would expect that the amount of the change at this point would be in proportion to the amount of acid to be neutralized, or in other words, to the concentration of the colloidal clay. Preliminary results obtained by Marshall and Powell in this laboratory indicate that this is true. The data plotted in figure 2 shows that as the concentration of the acid clay becomes greater the amount of potassium required for flocculation in the alkaline region also increases. These values were obtained by centrifuging immediately after the electrolyte had been mixed with the colloid and consequently the absolute amounts required are somewhat higher than in the previous series.

In much of the work on the flocculation of clay the valence of the electrolyte has been considered the most important factor. The results presented here indicate; (1) that the electrolyte requirement of a clay with any electrolyte can only be defined with reference to a definite pH value, (2) that the reaction of the clay determines the general type of curve obtained, (3) that the concentration of the clay is an important factor especially with alkaline flocculants, (4) that while the amount of various acids required for flocculation varies widely if expressed in total or titratable acidity, they all flocculate at about the same concentration of hydrogen-ions.

#### THE EFFECT OF HYDROGEN-ION CONCENTRATION UPON THE ABSORPTION AND EXCHANGE OF BASES

One of the earliest experiments that we have on the absorption and exchange of bases contains results which, in all probability, are due to differences in hydrogen-ion concentration. Thompson (32) in 1845 found that the amount of calcium and magnesium liberated from soils by  $(\text{NH}_4)_2\text{SO}_4$  was in every case considerably greater than the amount liberated by  $(\text{NH}_4)_2\text{CO}_3$  while the amount of  $\text{NH}_4$  absorbed was greater in the case of  $(\text{NH}_4)_2\text{CO}_3$ .

Lemberg (16), in 1870 working on silicate minerals, found an equivalent exchange of bases between minerals and solutions of neutral salts. With

alkaline solutions the free base was absorbed without any appreciable exchange of bases. A few years later in 1877, Van Bemmelen (2) made his classic studies on absorption by colloidal gels. Like Lemberg, he found that solutions having an alkaline reaction, either the free hydrate or the alkaline salts of weak acids, such as  $H_2CO_3$ ,  $H_3PO_4$ ,  $H_2B_2O_7$ , were absorbed more strongly by soils and by silica gel than the neutral salts of the same metals. With the alkaline solutions there was no appreciable exchange of bases. The alkaline salts of the weak acids were converted into the corresponding acid salts. With neutral salts, however, an equivalent exchange of bases was frequently observed.

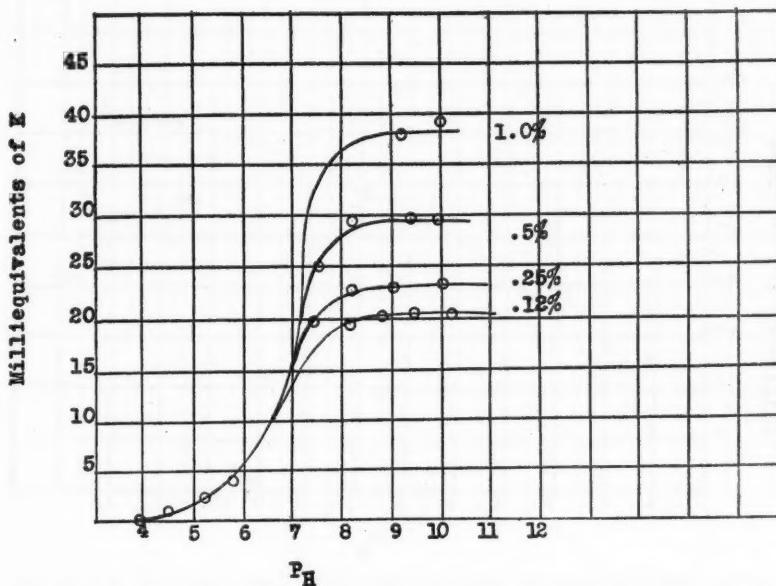


FIG. 2. THE EFFECT OF THE CONCENTRATION OF AN ACID COLLOIDAL CLAY UPON THE MINIMUM ELECTROLYTE REQUIREMENT WITH POTASSIUM MIXTURES AT DIFFERENT pH VALUES

Thirty years later Sullivan (29) studied the effect of a large number of salts upon a variety of silicates. In most cases some exchange of bases occurred but it was quantitative only in case a neutral mineral was treated with a neutral salt. The reaction of the mineral and of the salt solution used seemed to be the most important factors in determining the equilibrium. Unfortunately, we do not have very exact knowledge of the Sørensen value of his mixtures. The same criticism can be applied to much of the more recent work in spite of the fact that ready means of estimating the pH value of our mixtures are now available. In much of this work our knowledge of

the properties of the chemicals used and of the reaction of the soil enables us to see in a rough way how the hydrogen-ion concentration effects the equilibrium between chemical treatments and the soil. A typical case will be cited.

In his interesting study of base exchange in acid soils, Robinson (24) found that the supernatant liquid obtained by treating the acid soil with a 0.1 *N* solution of potassium acetate, contained much more titratable acid than that obtained with KCl or  $\text{KNO}_3$ . The acetate solutions contained in every case less salt after contact with the soil, while those of KCl and  $\text{KNO}_3$  showed more.

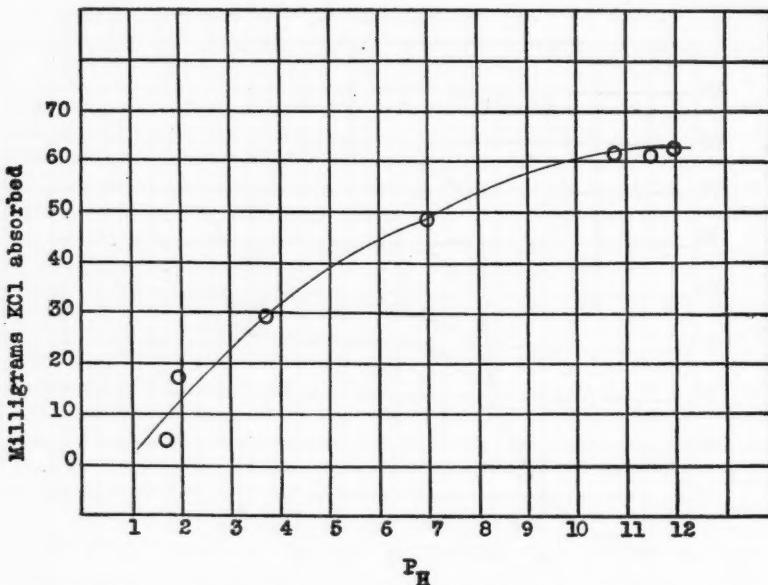


FIG. 3. THE EFFECT OF THE HYDROGEN-ION CONCENTRATION UPON THE AMOUNT OF POTASSIUM ABSORBED BY ONE GRAM OF AN ACID COLLOIDAL CLAY FROM .1 *N* POTASSIUM MIXTURES

We know that a potassium acetate solution is alkaline because of hydrolysis, and that a solution of KCl in equilibrium with an acid soil has a lower pH value than the soil itself. This would seem to indicate, as suggested by Robinson, that the differences might be due largely to the pH value at which equilibrium was established. If this assumption is true it should be possible to get similar results with KCl and mixtures of KCl and KOH combined in such proportions as to keep the potassium concentration constant and to gradually increase the pH value up to that of KOH. Such a study has been made in this laboratory using an acid colloidal clay and 0.1 *N* mixtures of KCl and KOH. The results are plotted in figure 3. As was anticipated,

the amount of potassium absorbed—as measured by the amount still in solution after equilibrium with the soil had been reached—increased almost linearly with the degree of alkalinity until a Sørensen value of about 10 was reached, then at a slower rate indicating that the saturation capacity for bases was being approached. A like study in which mixtures of  $\text{CaCl}_2$  and  $\text{Ca}(\text{OH})_2$  were used has been made in this laboratory by Cowan and similar results obtained. Starkey and Gordon (28) report similar results for the absorption of potassium by silica gel. Swanson (30) has recently reported almost identical results in his study of the effect of reaction upon the adsorption of calcium by soils.

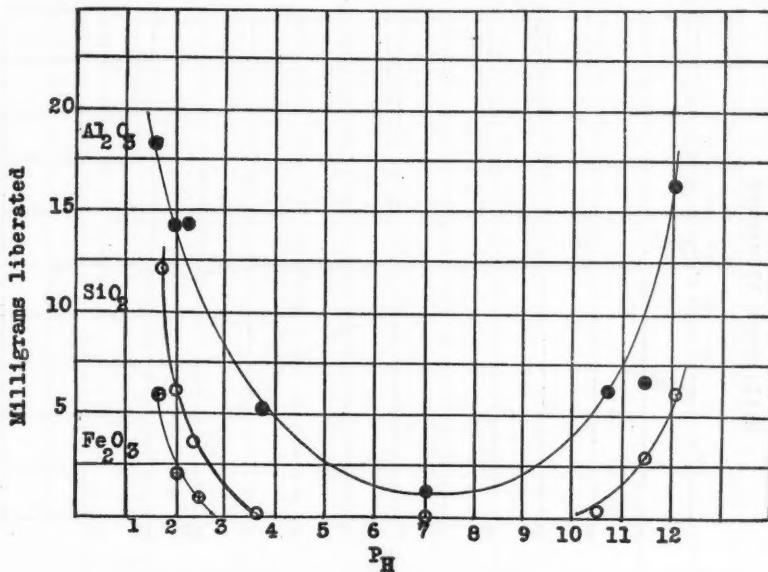


FIG. 4. THE EFFECT OF THE HYDROGEN-ION CONCENTRATION UPON THE LIBERATION OF  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  AND  $\text{SiO}_2$  FROM AN ACID COLLOIDAL CLAY BY .1N POTASSIUM MIXTURES

Analyses of the solutions for the other elements of the colloid made soluble by the mixtures of  $\text{KCl}$  and  $\text{KOH}$  also indicate the importance of pH control. The relationship for  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  is shown in figure 4. The curves are all similar in the acid region. The solubility decreases with a decrease in the hydrogen-ion concentration and becomes negligible around the neutral point. With further increases in alkalinity,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are again made soluble. The curves obtained by Cowan with mixtures of  $\text{CaCl}_2$  and  $\text{Ca}(\text{OH})_2$  are of the same type. The values for the calcium and magnesium liberated by the mixtures of  $\text{KCl}$  and  $\text{KOH}$  are given in figure 5. There seems to be no appreciable exchange of these bases in the more alkaline re-

gion. The solubility of the calcium in the alkaline mixtures was not the limiting factor, for  $\text{Ca}(\text{OH})_2$  could be added to the alkaline solutions in quantity without precipitation. Some evidence has been obtained which indicates that potassium may be liberated by  $\text{Ca}(\text{OH})_2$  if considerable more of the base is added than is needed to neutralize the acid clay.

If all the bases liberated are converted into their  $\text{KCl}$  equivalents, and the resulting values subtracted from the corresponding values for the amount of  $\text{KCl}$  absorbed, a curve can be obtained which will show the balance of bases at the different pH values. Figure 6 was obtained in this way. The values

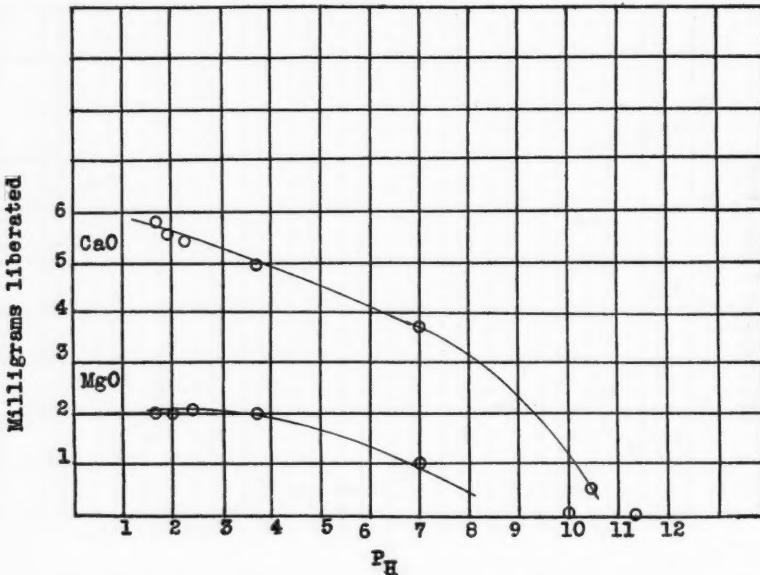


FIG. 5. THE EFFECT OF THE HYDROGEN-ION CONCENTRATION UPON THE LIBERATION OF  $\text{CaO}$  AND  $\text{MgO}$  FROM 1 GRAM OF AN ACID COLLOIDAL CLAY BY .1 N POTASSIUM MIXTURES

below the zero ordinate indicate that more cations have been liberated from the clay than have been exchanged or absorbed, equivalent exchange occurred at the zero ordinate, while those above this ordinate indicated that more base was absorbed than exchanged. It is interesting to note that the pH value at which the curve crosses the zero ordinate is the same as that of the clay.

Hissink (12) has pointed out the difficulty of determining the total base-absorbing capacity of a soil. The investigations cited above point out a reason for this complexity. The base-absorbing capacity of a soil can only be determined with reference to the hydrogen-ion concentration at which equilibrium between the soil and the salt or base has been reached. Hissink

(13), Swanson (30) and others have shown that there is no close correlation between the normal pH value of a soil and its base-absorbing capacity. The clay content of a series of soils is a better index to their relative absorptive capacities than their pH value. It is the titrable or potential acidity of a soil that determines its power for holding bases and this may have but little relation to the original pH value. McGeorge (20) has recently reported that

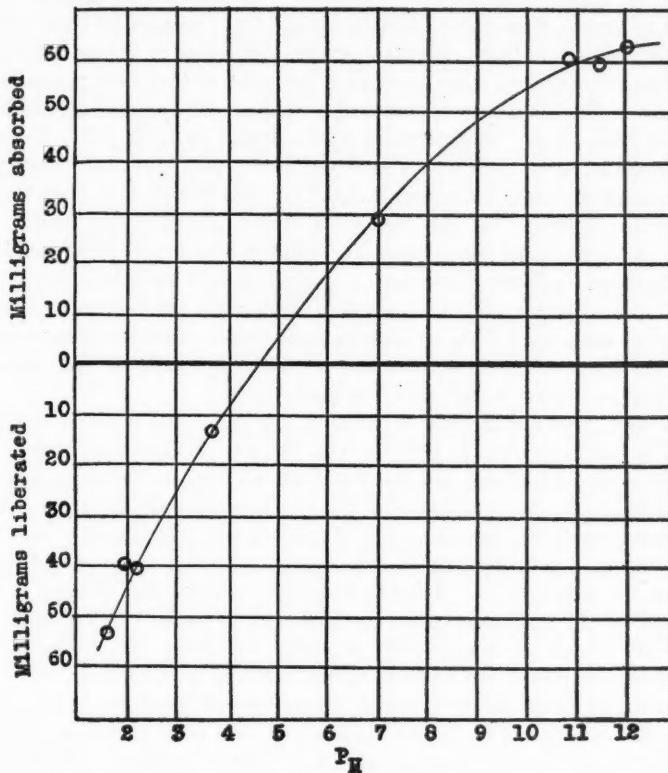


FIG. 6. THE EFFECT OF THE HYDROGEN-ION CONCENTRATION UPON THE TOTAL BASES LIBERATED OR ABSORBED BY AN ACID COLLOIDAL CLAY BY .1 N POTASSIUM MIXTURES. RESULTS CALCULATED ON BASIS OF KCl EQUIVALENT

two soils having an identical pH value, 5.98, differed by ten tons  $\text{CaCO}_3$  per acre in their titrable acidity as determined by the Veitch method.

Since the absorptive capacity of a soil for bases is greatly influenced by the concentration of hydrogen ions at which equilibrium is established, it is clear that the only proper way to compare the absorbing capacity of two soils is to measure that capacity at a definite hydrogen-ion concentration.

The failure to control this important variable has led to many disputes. The question of the liberatin of soil potassium by calcium has been investigated by scores of chemists and opinions vary widely. Plummer (23) in summarizing the literature before the American Society of Agronomy in 1921 stated that "all the experiments made have failed to show that basic compounds of calcium and magnesium increase by chemical action to any practical extent the solubility of the soil potassium." MacIntire (18) likewise concludes as a result of extensive lysimeter studies that "economical applications of burnt calcareous, burnt dolomitic, ground calcareous or ground dolomitic limestone will not effect a direct chemical liberation of native soil potassium" although he did obtain some liberation of potassium with excessive applications of these basic limes. Similar results were obtained by Lyon (17). Tressler (33), however, in his work on the same soil as was used by Lyon, found that while potassium was not liberated by  $\text{CaCO}_3$ , it was liberated by applications of  $\text{CaSO}_4$ . Erdman (10) and numerous others have reported similar results. A survey of the recent literature, including over a score of independent investigations, indicates then that in neutral or acid soils, basic salts like  $\text{CaCO}_3$  do not liberate soil potassium unless employed in great excess, while acid or neutral salts, like  $\text{CaSO}_4$ , do liberate appreciable quantities of potassium when applied in relatively small amounts. The importance of hydrogen-ion concentration control in such studies is quite evident.

The data presented in figure 6 indicates that all of the types of reaction noted by Van Bemmelen (2), Sullivan (29), Spurway (27) and others can probably be observed with any neutral or acid soil with any of the common bases and their salts by proper adjustment of the hydrogen-ion concentration. Any treatment which will increase the hydrogen-ion concentration of a soil will lower its capacity for holding bases because of the substitution of hydrogen-ions for the metallic ions. If the hydrogen-ion concentration of a soil is not changed by the treatment equivalent exchange of bases is to be expected. If the soil is more alkaline after the treatment, indicating that hydrogen-ions have been neutralized and replaced by the cation of the hydroxide, less than equivalent exchange will be observed. If just enough alkali is added to neutralize the acid it will be largely absorbed without basic exchange, while if a decided excess is added basic exchange may again be obtained. These views are in harmony with the mass law.

Let us consider the results to be expected from additions of  $\text{CaCO}_3$  and  $\text{CaSO}_4$  from this point of view. Calcium added as  $\text{CaCO}_3$  acts as a base and neutralizes the residual acidity in the soil thus raising its pH value. Since calcium ions replace hydrogen ions in the colloid complex there is no appreciable liberation of bases until the acidity is practically all neutralized. When calcium is added in the form of  $\text{CaSO}_4$  to a neutral or acid soil the hydrogen-ion concentration of the mixture is either unchanged or slightly lowered, consequently there is an approximately equivalent exchange of bases.

## THEORETICAL DISCUSSION

That the hydrogen-ion concentration exerts a profound influence in all physico-chemical studies of soils is a fact not to be questioned. When considering the probable theoretical mechanism of the observed facts, however, there may still be differences of opinion. Michaelis (21) has suggested that the surface molecules of a colloidal particle may be dissociated. Langmuir (15) considers adsorption as due to purely chemical residual valences. Hissink (14) and Van der Spek (26) are inclined to attribute the equivalent exchange of bases to chemical forces acting at the surface of the colloidal particle. Gordon (11) has presented a similar explanation for the behavior of silica gels. The work done in this laboratory on the colloidal fraction of acid clays shows (a) that standard hydroxide solutions when titrated with the acid clay solutions, give titration curves characteristic of weak polybasic acids by either the conductivity or the hydrogen electrode method (5); (b) that equivalent amounts of different bases are required for neutralization; (c) that the hydrogen-ion concentration of concentrated solutions of colloidal clay varies in the same way on dilution as with ordinary weak acids (6).

These studies seem to be further evidence of the chemical nature of the reactions of colloidal clay when coupled with the work reported in more detail above on (a) the relation of the hydrogen-ion concentration to the flocculation of an acid and a neutral clay, (b) on the effect of the concentration of the colloidal clay upon the variation in the amount of electrolyte required for flocculation at different Sörensen values, and (c) on the effect of the hydrogen-ion concentration upon the absorption and exchange of bases. Many results commonly cited as evidence against this conception may be attributed to the failure of the investigator to consider (a) the original reaction of the soil, (b) the hydrogen-ion concentration resulting after the soil and treatment have reached equilibrium with each other, and (c) the total or titrable acidity of the soil which is a complex function in which specific surface may play a larger rôle than the Sörensen value of the untreated soil.

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## ABSTRACTS OF SOME PAPERS ON SOILS AND PLANT PHYSIOLOGY PRESENTED OR PUBLISHED IN 1923

### RUSSIA<sup>1</sup>

A convention of the Russian investigators in soil science with the participation of geo-botanists, was held in Moscow during September 10-15, 1923. The following were elected as members of the Presidium of the All-Russian Convention; K. D. Glinka; A. A. Yarilov; N. M. Tulaikov; V. V. Hemmerling; Y. N. Afanasiev and B. A. Keller.

Thirty-five papers were presented, twenty-eight on questions of soil science and seven on geo-botanical subjects. A large number of the papers were devoted to questions of soil cartography; the others were devoted to the origin of soils, the study of properties of soils, methods of chemico-mechanical analysis, etc. Abstracts of some of the papers presented at the convention are given below.

#### On the Moisture Properties of the Soil. A. F. LEBEDIEV.

1. The soil and subsoil are enriched in moisture not only by atmospheric precipitation (rain, snow, fog, hail, etc.), but also by the water vapor of the atmosphere and the condensation of the water vapor moving from the lower depths toward the surface of the soil.

2. The enrichment of the soil moisture due to the water vapor of the atmosphere takes place by (a) molecular and (b) thermal condensation of the atmospheric vapor in the surface layers of the soil exclusively.

3. At 0°C. water exists in the soil in four conditions, viz., in the form of vapor, as hygroscopic meter, in a condition of films<sup>2</sup> and as gravitational water.

4. Hygroscopic, film and gravitational moisture are characterized by different elasticities of the water vapors and different modes of movement. (A) If the moisture is in the film or gravitational state, then the soil air, independent of the degree of saturation and temperature of the soil, has, in the first place, a maximum elasticity of water vapor for the given temperature (the relative humidity being 100 per cent). (B) In the case of hygroscopic soil moisture, the elasticity of the water vapors of the soil air does not reach the maximum saturation (relative humidity being less than 100 per cent) and depends both

<sup>1</sup> These abstracts were prepared by N. Tulaikov and M. Kuzmin, Agricultural Experiment Station, Saratov, Russia, and translated by J. S. Joffe, New Jersey Agricultural Experiment Stations.

<sup>2</sup> The author uses the Russian term "plototchnaya" and the true translation is film. The author does not mention capillary water. His term, however, may include this.—J. S. J.

upon the degree of saturation and on the temperature of the soil, diminishing at constant temperature with a decrease of the soil moisture, and increasing at constant soil moisture with an increase in temperature. (C) Hygroscopic water may move about in the soil only upon changing into a vapor state. (D) Film water moves in the soil in a liquid condition from places of a higher moisture content to those of lower. Gravity does not influence the speed of movement of the film moisture. (E) Gravitational waters move in the soil in a liquid condition, under the influence of gravity. (F) Film and gravitational waters move about in the soil also in the condition of vapor, at a uniform moisture content throughout the soil the movement takes place from areas of higher temperature to those of lower; at the same temperature, the vapor moves from layers of higher moisture content to those of lower.

5. It is necessary to distinguish daily and seasonal changes in the distribution of the vapor pressure in soils and sub-soils. As a result of the daily changes we have (a) loss of soil moisture by evaporation and (b) the movement of water in a vapor state from the upper soil strata to the lower strata and *vice versa* are a result of the daily changes. The decrease in the intensity of these processes may be attained in agricultural technic by means of surface mulching of the soil.

6. The water with which the soil is enriched as a result of molecular condensation (see paragraph 2) of the atmospheric vapor, in connection with what has been said in paragraph 5b, is a source of water physiologically useful to plants.

7. As a result of the seasonal distribution of the vapor pressure of the moisture in the soil and subsoil we have: (a) the movement of water, in a vapor state, during the winter period, from the subsoil to the surface; this increases the moisture content of the soil, which is in turn dependent upon precipitation during the fall-winter period; (b) the movement of water from the soil and the upper layers of the subsoil into the deeper subsoil, to strata with constant yearly temperature (summer period).

8. In the stratum having a constant yearly temperature during the summer period, the formation of liquid waters should take place at the expense of the water vapor, which moves toward this stratum from below and from above. These waters may feed the subsoil waters of the first horizon fully or partly depending upon the climatic and geologic peculiarities of the regions.

9. Below the stratum where constant temperature begins the elasticity of the water vapors of the subsoil remains at times unchanged (seasonal), increasing with depth. Due to this, there is a constant one-sided movement of the water vapor from the deeper layers of the earth's crust to the less deeper strata of the subsoil. In those places where the thermal gradient increases abruptly, there should be noticed the formation of liquid waters. These waters participate in the formation of subsoil waters of the second and third horizons and so on; whereby these horizons are probably often formed in the manner indicated.

10. The moisture-holding capacity of the subsoil, which has a homogeneous structure and considerable strength, varies at different heights.

11. If the strength of a homogeneous subsoil is great enough then its upper strata possess a moisture content corresponding to the "maximum molecular moisture-holding capacity" of the given rock species; on the other hand the moisture-holding capacity of the lower strata may be considerably higher than the above unit, at times even several times as high as in the case of sand, for example; although even in this case it does not reach the full moisture-holding capacity; the moisture-holding capacity of the intermediary strata of the subsoil changes constantly, diminishing from the lower to the higher strata.

12. In a homogeneous subsoil, the moisture content of which is not higher than the maximum molecular moisture-holding capacity, the hydrostatic pressure, caused by additional moistening of the subsoil, is not transmitted through strata with a moisture content described above.

13. In a homogeneous subsoil, the moisture content of which is greater than the moisture corresponding to the maximum molecular moisture-holding capacity, hydrostatic pressure is transmitted from some strata of the subsoil to others.

14. In homogeneous subsoils of great strength with an established equilibrium of water, an additional moistening of the upper strata calls forth a movement of a similar amount of water into the strata of the subsoils. This translocation is accomplished in the following manner: while the newly added water moves along the strata with a moisture content corresponding to the maximum molecular moisture-holding capacity, the equilibrium of the water in the lower strata of the subsoil is not disturbed (paragraph 12), and the water of the lower horizon of the subsoil does not leach out; however, equilibrium is disturbed as soon as the newly added water reaches the horizon with a moisture content greater than in a strata with a maximum molecular moisture-holding capacity, (paragraph 13); then during a certain period of time, the length of which is determined by the rapidity of transmission of the hydrostatic pressure in the given rock species, leaching of water from the lowest strata of the subsoil takes place.

15. Observations on the moisture content of the subsoils in nature show, in connection with the depth of the water table, amount of precipitation and energy of evaporation of water by plants and soil, that in northern regions the penetration of the precipitated waters up to the first horizon of the water table seems to take place during the greater part of the year. In the southern regions, the penetration of the precipitation adapts itself to a shorter period, the end of winter and beginning of spring. In the deserts with clay soils and subsoils, we may assume with sufficient probability of absence of the penetration of the precipitation to the first horizon of the water table.

16. In the low parts of the relief, the penetration of the precipitation to the first horizon of the ground waters may take place in all widths (in a horizontal plane?).

17. In the regions of sandy and fine sandy soils and subsoils, the penetration of the precipitation may reach the first horizon of the ground waters, independent of the location of the region, for the maximum molecular moisture-holding capacity of such soils is very small and the penetration of the water in such soils takes place relatively fast.

18. In soils which are not of a homogeneous character, the waters are distributed at equilibrium in a different manner than in the soils of homogeneous structure (paragraph 11); however, this does not change the conditions established in paragraphs 12, 13, 14.

19. The penetration of precipitation apparently is possible down to second and third horizons of the ground waters and so on, if the layer of the ground waters possesses some penetrability and the hydrostatic pressure of the ground water is sufficiently great to overcome the forces of resistance, which develop with the movement of the water both in the impervious layer as well as at the contact points with the underlying strata.

20. The ground waters are formed both by condensation of the water vapor of the soil, subsoil and juvenile waters, and also by the infiltration of the liquid waters (precipitation, ground waters of the overlying horizons.) Apparently it happens more often that these processes take place simultaneously, superimposing one another. However, there are in nature undoubtedly also such conditions when the ground waters are formed by condensation exclusively. In either case the ground waters must find themselves on a relatively pervious layer. In the latter case the condition of the ground water may not correspond with the condensation layer, where liquid water is formed from water vapor.

*Origin of Alkali Soils.* D. G. VILENSKY.

1. All salinized soils begin with the salines (solontshaki) which originate in the zones where the evaporation is greater than the atmospheric precipitation; in places where the water table is raised to the surface, as a result of which the capillary rise brings up water-soluble mineral salts and concentrates them at the surface. The sources of the salts are either the parent rocks, if they contain salts, or the ground waters if they contain in solution mineral substances.

2. The alkali soils differ from normal soils not only by the presence of large amounts of salts, but also by the properties of the zeolitic portion. When sodium salts enter the soil an absorption of sodium, by the zeolitic substances takes place, and if such a soil loses its salts it will not return again to its original condition, for its zeolitic (and humic) portions will contain even after the removal of the excess of sodium salts from the soil solution, certain amounts of zeolitic sodium.

3. All the above groups of soils containing salts represent the product of metamorphosis of salines and originate from them after the contact with the ground waters, which feed them, ceases. The washing of the salines by atmospheric precipitation as well as the removal of the salts from the surface horizons into the lower depths takes place first, then the alkalization of the surface

begins, due to the formation of sodium carbonate as a result of washing. According to Gedroitz, this sodium carbonate is formed at the expense of the zeolitic sodium as a result of double exchange of calcium carbonate and the zeolitic portion. After the electrolytes are washed out and the formation of sodium carbonate has begun, the semi-reversible colloids of the soil change into sols and, by passing downward they clog up the capillaries and create at the surface of the soil conditions of temporary excess of moisture; these conditions are among the main causes of the continuance of the metamorphosis of these soils.

4. In the post tertiary valleys of Eurasia (European Russia), the saline soils which later gave rise to alkali soils were formed during the dry postglacial epoch when the dry and warm climate and the prevalence of lakes, high level of river waters and ground waters favored the formation of local accumulations of water soluble mineral salts in the upper layers of the subsoils. Thus the alkali soils are a derelict formation chiefly of the postglacial epoch. This does not exclude their possible formation in our times, especially at the outcrops of parent rocks containing salts.

5. Those groups of alkali soils which we may observe now represent separate stages of a process of gradual metamorphosis of salines, under conditions of various climatic zones. The geographic regularity of their distribution in the valleys of Eurasia indicates the direction of this metamorphosis.

6. In our present geologic epoch, in the zones of the dry steppes, the tshernoziems, forest steppes, and finally in the forest zone, an active process of a gradual decomposition of the soils containing salts is going on under the combined influences of the waters standing on their surface, the accumulations of meadow and marsh vegetation, and the oncoming forest. The final result of all these factors is the conversion of alkali soils into degraded soils, which, in their outer appearance, resemble the podzols of the forest zone.

*On the Amelioration of Salinized Soils.* D. G. VILENSKY.

1. Notwithstanding the great number of theoretical investigations and practical experiments conducted largely in the United States, the problem of amelioration of soils containing salts cannot be considered as solved even in its first stages. This is due chiefly to the fact that there is no satisfactory understanding of the origin of such soils.

2. The new theory of the origin of alkali soils makes it possible to draw several conclusions which are interesting from the standpoint of amelioration of soils containing salts. From the standpoint of this theory, one of the main routes to the solution of this problem is the study of the process of degradation of alkali soils and the great experiment of the destruction of these soils which nature itself has performed in our present epoch.

3. Measures of radical amelioration of alkali soils without irrigation, known at the present time are mechanical removal of the structural horizon; the addition to the alkali soils, in the process of their cultivation, of manure, peat,

leaves, marsh and acid meadow soil, probably certain mineral fertilizers of an acid reaction, as superphosphates, and lastly, green manuring. These measures are directed towards enrichment of the alkali soils with organic materials which are to undergo decomposition at times of excessive moisture.

4. The measures which may be taken to prevent the formation of saline soils under irrigation are: preventing the rise of the water table; leaching the salines with the purpose of lowering in them the concentration of easily soluble salts; regular measures to counteract the harmful effects of leaching such as an increased basicity and extremely undesirable physical properties. The planting of appropriate shade trees and shrubs along irrigation canals may be recommended for shading the soil and tending to preventing the rise of underground waters.

*The Absorbing Power of Soils and the Principle of Automatic Self-Irrigation of Soils.* B. G. KORNEV.

Soils possess the ability to absorb water with a certain power. Until now, the nature and power of this property has not been studied. In the spring of 1921 the author constructed an apparatus which measures this power with a mercury manometer. The work with this apparatus in measuring the absorbing power made it possible to establish the following:

The absorbing power of the soil is free energy which may be utilized for irrigation purposes. In the main, the system of automatic irrigation (used by the author) consists in the following:

1. The absorbing power of soils varies with different soils depending on structure, degree of compactness, size of the mechanical particles of the soil and degree of soil moisture. Thus the absorbing powers of the soils studied were expressed by the following manometer readings: heavy compacted loam, 51 cm.; non-compacted loam, 46 cm.; fine compacted sand, 40 cm.; fine non-compacted sand, 33 cm.

2. The absorbing power of soils varies inversely with the degree of soil moisture. At optimum moisture, the power of absorption practically ceases, and at full moisture-holding capacity approaches 0.0 cm. Thus, for instance, for a heavy loam:

|                  |        |        |        |        |         |       |
|------------------|--------|--------|--------|--------|---------|-------|
| Moisture:        | 2%     | 16%    | 23%    | 27%    | 32%     | 40%   |
| Absorbing power: | 51 cm. | 24 cm. | 16 cm. | 10 cm. | 0.5 cm. | 0 cm. |

and for a fine sand:

|                  |        |        |        |       |       |
|------------------|--------|--------|--------|-------|-------|
| Moisture:        | 2%     | 7.6%   | 13%    | 16.3% | 28%   |
| Absorbing power: | 30 cm. | 17 cm. | 10 cm. | 3 cm. | 0 cm. |

3. The apparatus used may serve as a standard for the measurement of the soil moisture.

4. The absorbing power of the soil is a surface energy phenomenon of the soil particles.

5. The optimum content of soil moisture is a constant unit for each soil corresponding to the moment of change of film water into liquid drops.

Special porous tubes are placed in the soil. They are united into one closed net work and are filled with water. The walls of the tubes become saturated with the water. The soil, due to its power of absorption, begins to absorb the water from the tubes and becomes moist. As a result, a change in pressure takes place, and water from the lower lying reservoir rises through the main tube of the system and makes up the loss. The height to which the water

rises may reach six to seven meters. When the soil is saturated with water the absorbing power falls and the income of water ceases; in the case of over-saturation, the excess of water goes back through the pipes into the reservoir and the irrigation system works like a drainage system. A constant definite per cent of moisture may be established by this method of irrigation, as the soil itself serves as a regulator.

Following the principle of utilization of the soil's absorbing power for irrigation purposes, pot experiments were started with an automatic self-irrigating system. The vessels consisted of two pots, an inner porous pot and an outer impervious pot. The water is placed between the two pots; when the soil is placed in the inner pot, the water is absorbed by the soil through the walls of the porous pot and becomes moist; a lowered pressure results within the vessel as a result of which the water from a feeding reservoir flows automatically towards the space between the two vessels, making up the loss. A whole series of such vessels may be thus arranged with one reservoir, and the soil is then moistened automatically. By lowering the water level in the reservoir, the percentage of moisture may be changed in the pots.

*The Root System of Grasses in Soils of the Podzol Type.* G. A. KATSHINSKY.

On soils of the podzol type, the grasses develop the chief mass (about 90 per cent) of large and small roots in the plowed horizon. The podzol under-horizon, unproductive in composition and unfavorable on account of its physical properties, serves as a hindrance for root development which is hard to overcome. In the compact underhorizon which is alluvial, the roots penetrate along the crevices and worm borings, not forcing independent paths through the soil. The soil in such cases presses on the roots.

*The Characterization of the Main Soil Types from Data of Absorbed Bases.*

V. V. HEMMERLING.

A clear understanding of soil-forming processes cannot be gotten simply by a study of the morphology of soils. The searching of the paths of this process should be chiefly a static study. A total analysis or extractions with hydrochloric acid do not give a satisfactory characterization of a soil. The absorbed bases—the most mobile and active part of the soil—which are present either in solid or liquid phase, may give well defined data for the determination of the genesis and broad characterization of soil types. The author illustrated his paper with a large series of charts, which characterized the various soil types according to the content and distribution of the absorbed bases.

*The Differentiation of Podzol Soils by Morphological Indices.* A. A. KRASIUk.

The following indices were presented by the author as a basis for identification of podzol soils.

1. The absence of a moist immobile atmosphere over the soils indicate good insulation [*literal translation—ED.*]

2. Gray or dark gray color of the rocks. A tensile strength not less than 14 cm.
  3. Slightly granular, lumpy, nut-like structure of the rocks. Traces of digging animals.
  4. Weak podzolization or slight loss of bases of the rocks. The stratified structure is not clearly expressed.
  5. Medium loam as a subsoil; porous and with a large nut like or prism-like structure.
  6. Presence of carbonates.
  7. Absence of sharply expressed ortstein or alluvial horizon and the presence of a moderate quantity of boulders.
  8. Apparent, gradual, and wide sloping. Peculiarities of exposure: slightly rolling relief or slightly sloping water sheds.
  9. Absence of sharp coloration of the plow zone.
- On the basis of these indices, the podzol soils were classified according to their productiveness into ten groups.

#### GERMANY\*

The papers discussed in this section have all appeared since the publication of the fourth edition of Bodenkunde für Land- und Forstwirte, 1923.

#### *Investigations in Soil Physics*

The work done by Ferd. Zunker and G. Krauss concerns soil structure (*Landwirtschaftliche Jahrbücher*, v. 58, p. 159-203; and *Internationale Mitteilungen für Bodenkunde*, v. 13, p. 222.) Both investigators use Wiegner's method for the determination of the suspension curve which represents the sedimentation of soils suspensions per time unit. From these data they try to find the total soil area. In the most recent work of Johannes Rothe (*Landwirtschaftliche Jahrbücher*) it is, however, pointed out that this is impossible notwithstanding Zunker's ingenious calculations. This is obvious because the fundamentals of the suspension analyses cannot be considered to be satisfactory for this purpose. A paper from G. Hager deals with the changes in soil structure, which he thinks are caused by colloid-chemical phenomena. (*Zeitschrift für Pflanzenernährung und Düngung*, part A, v. 2, p. 292-311.)

Hans Götsch (Dissertation, Kiel, 1922). Georg Ruhnau (Dissertation, Königsberg, 1922), and Bernhard Szonn (Dissertation, Königsberg, 1923) studied the behavior of the soil to water.

Götsch found that the ascent of water in vertical tubs can be represented by the following equation:

$$t = \frac{8n}{\pi^2 g} \left( 2.302 h \cdot \log \frac{h}{h-x} - x \right)$$

\* These abstracts were prepared by Eihl. Alfred Mitscherlich, Albertus University, Königsberg, Prussia, and translated by N. Mogendorff, New Jersey Agricultural Experiment Stations.

In this equation  $h$  = height of ascent

$x$  = momentary height of ascent during time =

$g$  = gravity

$n$  = coefficient of internal friction

(coefficient for water at 15°C. = 0.0115)

2.302 = modulus

$r$  = radius

Göttsch remarks that in experiments performed by Von Seelhorst the soil water did not rise to the surface by capillary action. Soil cultivation did not influence the water evaporation, the latter being the same for compact and non-compact soils. This was true for his own experiments as well as for Von Seelhorst's.

Ruhnau studied the relation of sandy soils of different fineness to water. The size of the particles was found by determining weight and specific gravity of a great number of them. He worked chiefly with a quarry sand and a sea sand and determined water capacity, water permeability, water ascent and water evaporation in these sands.

Szonn determined the size of the particles in the same way and found the following relationship between the water permeability and the size of the particles:

$$\text{For a sea sand: } \log (33.36 - y) = \log 33.36 - 5.3x$$

$$\text{For a quarry sand: } \log (39.85 - y) = \log 39.85 - 4.3x$$

$x$  = size of particles in cubic centimeters

$y$  = required quantity of water in cc. per minute per square centimeter of filtration surface

The differences in the constants are due to the different shapes of the particles.

Szonn mixed the soil with varying amounts of sand (with a maximum of 80 per cent sand) and found that the required quantities of water ( $x$ ) increased with the percentage ( $y$ ) sand in the soil, in the following way:

$$\text{For a loam soil: } \log (80 - y) = \log 80 - 1.5(x - 0.20)$$

$$\text{For a peat soil: } \log (80 - y) = \log 80 - 1.5(x + 0.58)$$

A splendid contribution to the knowledge of soil cultivation has been given by Otto Born (Inaugural Dissertation, Königsberg, 1923). He improved Von Schermbeck's soil probe by supplying a device registering the energy produced. He determined the energy required for different soil types as a function of the water content and also as a function of the air space in the soil.

#### *Investigations in Soil Chemistry*

Engels (Zeitschrift für Pflanzenernährung und Düngung, part B, v. 2, p. 185-209) gives us a general study on the solubility of soil plant food in relation to fertilization.

J. König, J. Häsenbaumer, and J. Schäfer (*Landwirtschaftliche Jahrbücher*, v. 58, p. 55-124) try to find the relationship between the plant food present in the soil and the food taken from it by potatoes. They state that 1 kgm. of normal potatoes should contain 25 gm. of potassium, 18 gm. of nitrogen and 6 gm. of phosphoric acid. An abundance of these foods in the soil is indicated if the potatoes grown upon it contain larger amounts of these elements while the soil is considered deficient if lower amounts are found in the potato crop. Such data will permit only a rough estimate because, according to the results obtained by the reviewer, the food taken up by the crop depends not only upon the plant-food contained in the soil but also on other factors determining the total yield. More attention has been paid to these facts in a later publication by J. König and J. Hasenbäumer entitled "Die Ermittlung des Nährstoffbedarfes der Pflanzen und des aufnehmbaren (ausnutzungsfähigen) Nährstoffvorrats im Boden" (*Landwirtschaftliche Jahrbücher*, v. 59, p. 97-126).

Eilh. Alfred Mitscherlich shows in his paper "Der Düngungsversuch" (*Landwirtschaftliche Jahrbücher*, v. 58, p. 125-158) how the records obtained from fertilizer experiments in the field can be made to agree with pot experiments. He suggests a method for transforming the records of pot experiments for field use. In a second paper he shows how it is possible to determine by means of pot experiments, the quantity of available plant food present in 100 gm. of soil (*Landwirtschaftliche Jahrbücher*, v. 58, p. 601-617). The law of the growth factors as established by the writer is the fundamental principle for these studies. In a third paper, prepared in coöperation with H. Wagner, the increase of yield caused by increasing applications of potassium and magnesium was studied (*Landwirtschaftliche Jahrbücher*, v. 58, p. 645-652). The investigators who used sand cultures for their experiments state that magnesium causes an increase in yield only where there is a real lack of magnesium in the soil. A favorable side effect (*Nebenwirkung*) could not be observed under these conditions.

Still further objection is made by O. Lemmermann and Paul Ehrenberg against the system of Aereboe-Wrangell which was proposed for the purpose of saving phosphoric acid. The question of reaction in connection with phosphoric acid fertilizers is also discussed extensively (*Zeitschrift für Pflanzenernährung und Düngung*, part B, v. 2, p. 73-91, 129-136, 408-423).

Münster reports on the influence of alkaline soil reaction on production (*Zeitschrift für Pflanzenernährung und Dungung*, part B, v. 2, p. 289-298). He shows that the application of the stronger alkaline fertilizers does not do as much harm to heavy as to light soils. A loam soil should not contain more than 0.35 gm. soluble alkali per kilogram, while this amount should not exceed 0.20 gm. in the case of a sandy soil. The sensitiveness of different plants may differ very much.

Gering and Sander showed in their study on soil acidity (*Zeitschrift für Pflanzenernährung und Düngung*, part B, v. 2, p. 299-314) that the action of the acidity differs very much for different plants. Even the same acidity may

influence the same crop in different ways. Therefore, great care should be taken in judging the relationship between soil acidity and plant growth.

Further investigations on the influence of carbon dioxide on plant growth were made by Paul Spirlgatis, who showed that an increase of the carbon dioxide content of the air could give an increase in yield only if the light factor were depressed (Botanisches Archiv. Verlag des Repertoriums, Dahlem bei Berlin, v. 4, p. 381-403, Inaugural Dissertation, Königsberg i. Pr. 1923).

A. Densch and Th. Hunnius (Zeitschrift für Pflanzenernährung und Düngung, part B, v. 2, p. 241-252) studied the action of increased carbon-dioxide supply in the field. An increase in yield due to carbon dioxide was not observed.

Otto Lemmermann (Zeitschrift für Pflanzenernährung und Düngung, part B, v. 2, p. 142-146) experimented with rye using different quantities of seed per unit and fertilizing in different ways. The records obtained in the different years were not the same.

#### THE NETHERLANDS<sup>4</sup>

*Investigations on Nitrification and Denitrification in Tropical Soils.* F. C. GERRETSEN. Archief Suikerindustrie Nederlandsch Indie 1921, vol. 29, pp. 1397-1530.

The primary purpose of this investigation was to study the relation existing between the fertility of several sugar cane soils and rice soils and the nitrification and denitrification in these soils. It was shown that important differences can exist in the nitrifying power, while these differences do not influence the general appearance of the sugar cane. The crops appeared poor without any exception when denitrification took place in the natural soil to which only nitrate was added. Extracts were obtained from a number of infertile soils in which the nitrification was delayed for several weeks. This was caused by toxic substances which disappeared when the soil was thoroughly aerated.

These substances could also be removed from the extracts by shaking with a well aerated soil. As a rule, poor nitrification is found in good rice soils on account of their wetness. A considerable amount of nitrate-nitrogen, which remains in the soil after the sugar cane has been harvested, is lost every year through denitrification in the wet sands. Nitrite formation after fertilizing with ammonium sulfate seemed to depend on the hydrogen ion concentration. Nitrate formation was not detectable when the reaction was more acid than pH 7.2, nitrate formation then going on faster than nitrite formation. A typical reduction of iron compounds shows itself in soils which have been submerged for some time. In "sawahs" this is indicated by the presence of a blue color which disappears again when the soil is aerated. FeS was not present in these soils. A measure of the aeration appeared to be the proportion of the amount of iodine which were liberated from an acidified solution of potassium iodide by the same soil before and after aeration.

<sup>4</sup> These abstracts were prepared by D. J. Hissink, Agricultural Experiment Station, Groningen, Holland; and translated by N. Mogendorff, New Jersey Agricultural Experiment Stations.

*On the Occurrence of a Bacteriophage in the Nodules of the Leguminous Plants.*

F. C. GERRETSSEN, A. GRYNS, J. SACK, AND N. L. SÖHNGEN. Centralblatt für Bacteriologie, Part 2, v. 60, P. 311.

Bacteriophage were isolated from the nodules of clover, lupines and serradella and were also obtained from the stalks and roots of these plants. Possibly this might give an explanation for the way in which the bacteria are dissolved in the nodules. The lytic action is very specific, e.g., the serradella bacteriophage does not dissolve the bacteria of the lupines. Bacteriophage could be isolated directly from farm and garden soil, but they could not be obtained either from heather or forest soil. The resistance of the bacteriophage to the rays of ultra-violet light is at least eight times as great as for the bacteria concerned.

*Report on the Investigation on the Causes of the Poor Appearance of Some Crops in Zeeland.* D. J. HISSINK AND K. ZYLSTRA. Verslagen van Landbouwkundige Onderzoeken der Rykslandbouw Proefstations (Reports on the agricultural research work of the State Agricultural Experiment Stations), 1922, no. 27, p. 1-12.

The poor appearance of some crops (beets and alfalfa) during the abnormally dry summer of 1921 was considered to be due to inadequate water supply to the bad spots of the surface soil, especially where sandy layers occurred near the surface.

*Studies on Samples of Soil and Dredged Mud from the Polders and Lakes East of the Utrechtse Vecht in Connections with the Draining Plans of These Lakes.* DR. D. J. HISSINK. Internationale Mitteilungen für Bodenkunde, v. 11, p. 166-183.

This is a contribution to the knowledge of the chemical composition of bottom peat soils.

*The Black Clay of Thesinge (in the province of Groningen Holland).* CHR. BROCKMANN AND D. J. HISSINK. Verhandelingen van het Geologisch-Mijnbouwkundig Genootschap voor Nederland en Kolonien, geologische serie, v. 6, p. 43-55.

The black clay lies on the top of alluvial North Sea clay; for this reason it cannot be potters' clay (Launenburger Ton von Schucht) though it resembles the latter strongly. It differs from potters' clay, however, by its content of diatoms and other organic residues.

*A Simple and Quick Method for Determining Soil Acidity.* D. J. HISSINK. Chemisch Weekblad (1922), v. 19, p. 281-283.

The method Comber used for recognition of acid soils (treatment of 2 gm. of air-dry soil with 5 cc. of a 4 per cent solution of KCNS in 95-96 per cent alcohol) was applied to a great number of different soil types; the pH value of an aqueous suspension of these soils had been determined with the potentiom-

eter. These comparative determinations showed that a satisfactory relation existed between the potentiometrical pH value and the red color obtained by shaking Comber's reagent with the air-dry soil. In most cases, sufficient accuracy was obtained when the soil acidity was estimated by the red tint. Simple instruments and a color chart have been placed at the disposal of the farmers.

*Some General Conceptions on Acidity and the Rôle Played by It in Several Processes.* DR. D. J. HISSINK. Verslagen van Landbouwkundige Onderzoeken der Rykslandbouw Proefstations (1922), no. 27, p. 133-145.

An understanding of soil acidity and its probable influence on plant growth can be had only when the acidity of a solution is defined in scientific terms, when it is known how the acidity is expressed by figures and which factors influence it. This article tries to explain these facts to well trained farmers.

*The Acidity of the Soil.* D. J. HISSINK AND JAC. VAN DER SPEK. Verslagen van Landbouwkundige Onderzoeken der Rykslandbouw Proefstations (1922), no. 27, p. 146-161.

This paper consists of six sections as follows:

1. The components of the soil affecting soil acidity, namely, carbon dioxide, calcium carbonate, clay and humus substances. It is argued that the acidity of an aqueous soil suspension is determined by the number of adsorptively bound hydrogen ions present in the outside layer of the electric double layer surrounding the particles. Therefore, this acidity will depend upon the saturation condition and upon the extent to which the soil acids are dissociated (clay acids and humus acids).

2. Investigations on the acidity of Dutch soils: The pH value of the aqueous soil suspensions were determined potentiometrically. Soils containing calcium carbonate were faintly alkaline with an average reaction of about pH 7.5. The reaction of the humus soils (bottom peat soil, upland peat soil, humus clay soil, humus sandy soil) was between pH 3.5-4.0 and pH 8. The reaction of the clay soils with little or no humus was between pH 6.0 and pH 8.0. There was a relationship between the hydrogen-ion concentration and the lime content calculated of the clay and humus.

3. Relationship between soil acidity and plant growth: It is claimed that the need of lime is closely related to the optimum acidity for any given soil and for any given crop.

4. The changes in soil acidity: The changes in the pH values due to the influence of different salts are discussed and explained.

If, for instance, a soil is treated with a solution of potassium chloride the K ions are exchanged not only for Ca, Mg and Na ions, but also for the adsorptively bound hydrogen ions of the soil.



Through this reaction the acidity of the solution will increase and the soil acidity will decrease. The acid solution acts on the compounds of aluminum and iron in the soil, dissolving relatively large amounts if its strength is sufficient. When the soil is treated with solutions of salts derived from weak acids, e.g., potassium acetate, the equilibrium



will be moved far to the right in consequence of the slight dissociation of the acetic acid. The pH value changes only slightly, but when the filtrate is titrated with alkali rather high titration figures can be obtained. If a soil is treated with a solution of potassium chloride the real acidity (hydrogen-ion concentration) is greater and the titration figure (number of cubic centimeters of alkali needed for neutralization) is smaller than when the same soil is treated with a solution of potassium acetate. For figures concerning these investigations the reader is referred to the next abstract.

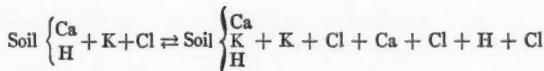
5. Relationship between the saturation point and soil acidity. This relationship is observed for a collection of clay humus soils.

6. Buffer condition and buffer value of the soil. The conception of buffer condition is generally discussed and explained.

*The Action of Solutions of Neutral Salts on Soil. A Contribution to the Knowledge of Soil Acidity.* JAC. VAN DER SPEK. Verslagen van Landbouwkundige Onderzoeken der Rykslandbouw Proefstations (1922), no. 27, p. 162-202.

In the first section a review is given of the prevailing opinions on the action of solutions of neutral salts on soils, resulting in an acid reaction of these solutions. In the second section the apparatus of the hydrogen electrode is discussed and also the way in which the pH values of the soil suspensions are determined by this device. Section 3 contains the results of the action of a 10 per cent solution of potassium chloride on about twenty soils of different types. The pH values found for the aqueous suspensions and for the KCl suspensions of these soils showed that all KCl suspensions of the acid, neutral and alkaline soils were more acid than the aqueous suspensions. Therefore all soils treated with the KCl suspensions of the most acid soils contained detectable quantities of aluminum and iron.

In view of these results it must be concluded that the colloidal particles of clay and humus of all soils contain adsorptively bound hydrogen ions as well as the adsorptively bound Ca, Mg, K, and Na ions. These adsorptively bound hydrogen ions can be replaced by other cations. When a soil is treated with a solution of a neutral salt such as potassium chloride a chemical reaction must take place between the adsorptively bound ions of the soil (Ca, Mg, K, Na and H) and the free ions of the solution. This reaction may be represented by the following equilibrium equation:



In this equation, Mg, K, or Na may be substituted for Ca. From this equation it can be concluded that the quantity of cations exchanged is influenced by the concentration of the salt solution used.

This has indeed been observed as a fact by several investigators, (Way, Aberson, and Harris among others) who found also that this exchange takes place according to the adsorption isotherm as the concentrations of a salt solution increase. It is observed, moreover, that the process of exchanging cations is not only influenced by the concentration of the salt solution used, but also depends on the kind of salt used for the solutn. This was especially studied for KCl, KCNS,  $\text{K}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOK}$  and  $\text{CaCl}_2$ . The results obtained with these salts could be interpreted by the equation given above. It is further pointed out that the phenomena observed, when soils are treated with solutions of neutral salts can indicate a chemical reaction (the exchange of equivalent quantities of the cations Ca, Mg, K, Na, and H; the progress of reaction in case a more or less dissociated substance is formed) or an adsorption phenomenon (the equilibrium is represented by the adsorption isotherm; the action of the different salts with the same kation or anion). It is undoubtedly a fact that a reaction takes place between the free ions of the solution and the adsorptively bound ions of the soil. On account of these facts the opinions existing about the action of neutral salts on soils could be made to agree, if adsorption phenomena were considered to be chemical reactions between the free ions the adsorptively bound ions. In this case the expression "adsorptively bound" should be understood to refer to ions situated on the surface of colloidal particles, practically not washed out by water, but exchangeable for other ions of the same electric charge. In section 4, Kappen's extended investigations on soil acidity are discussed also in connection with the theory developed on the action of salt solution on the soil. Section 5 deals with the formation of adsorptively bound hydrogen ions in the soil; and section 6, with the claims that the colloidal clay and humus particles contain adsorptively bound hydrogen ions.

*The Influence of Acid and Alkaline Fertilizers on the Growth of Crops. (Six Years of Practical Experience on the Plots of Spitsberger.) J. HUDIG AND C. MEYER. Verslagen Landbouwkundige Onderzoeken Rykslandbouw Proefstations (1922), no. 26, p. 60-68.*

The conclusions drawn by these authors are:

1. Acid fertilizers should not be applied on acid soils (except for potatoes).
2. Leguminous plants either do not grow on acid soils or their growth is insufficient. They demand slightly alkaline or neutral soils.
3. Potatoes require a slightly acid soil.
4. It can be determined by means of laboratory research whether a soil requires a dressing of lime for neutralization or not; and if lime is required, the quantity needed.

*The Potato Scab in Its Relation to Climate and Soil.* H. M. QAUNJER AND J. HUDIG. *Cultura, Jaargang 35* (1923), p. 1-12.

A relationship was observed between soil acidity (pH value) and the scabby character of potatoes. The scab occurred on slightly acid and on alkaline soils. No scab, or only a very slight amount of scab was observed on soils with pH values of 5.5-5.0 or less. The dry year of 1921 proved to be a very severe scab year.

*Soil Water Level, Capillarity and Evaporation.* J. F. LICHTENBERG. *Cultura, Jahrgang 34* (1922), p. 262-270.

The writer points out the great importance of understanding the relation between the movement of soil water and the draining of the Dutch polders. The necessity of studies in the line of soil physics is emphasized.

*The Influence of Soil Type and Fertilization on the Nitrogen and Ash Contents of Our Farm Crops.* J. G. MASCHHAUPT. *Verslagen van Landbouwkundige Onderzoeken der Rykslandbouw Proefstations*, no. 27 (1922), 10th communication, no. 28 (1923), 11th and 12th communication.

The replacement of potash by sodium is discussed in connection with information given about mangolds. It is shown that potassium and sodium, and calcium to a less extent, can partially replace one another in equivalent quantities.

